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ACYLATION OF AMINO STILBENE SULFONIC ACIDS

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This invention is concerned with the preparation of certain stilbene derivatives. More particularly, it relates to a process for acylating amino sulfonic acids of the stilbene series. Specifically, the invention is concerned with an improved acid binder for the hydrogen halide acid which is formed in acylating amino stilbene sulfonic acids with an aroyl halide.

Amino stilbene sulfonic acids, especially 4,4'-diamino-stilbene-2,2'-disulfonic acid, are important dyestuff intermediates. In addition, it has been found more recently that several of the acyl derivatives of the latter possess special properties. They are highly effective "optical bleaching agents" or "brighteners" in overcoming the yellowish cast, which is found in, or developed by, many so-called "white" cellulosic materials.

A number of methods, none wholly satisfactory, have been suggested for the preparation of these acylated derivatives. In the past, the greatest difficulty has been that direct acylation with an acid halide cannot be accomplished particularly well, either in an aqueous medium solution or in an organic solvent. More recently, an improved method has been developed. An aqueous medium is used, the medium containing in addition to water, specified proportions of certain ketonic solvents.

Whatever the particular process used, so long as a reaction is carried out between an aroyl halide and an amino-stilbene sulfonic acid, a hydrogen halide acid corresponding to the aroyl halide is formed. This acid must be taken up or neutralized in some way, in order that the reaction product may be successfully formed and subsequently recovered. It is with the solution of this acid removal problem that the present invention is concerned.

In general, in cases of this kind, there is considered to be little choice between acid-accepting agents. It would ordinarily be presumed that an agent such as soda ash or an agent such as potash, would be substantially interchangeable. Accordingly, because soda ash is more commonly available, and ordinarily considerably cheaper, it is regularly used.

In attempting direct acylation of 4,4'-diamino-stilbene-2,2'-disulfonic acid with a benzoyl halide, such for example as ortho-methoxy benzoyl chloride, it was found that a large excess of the acid halide is required. This makes the process both expensive and wasteful. It complicates product isolation and purification, which must be carried out in the presence of relatively large amounts of the aromatic acid resulting from

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hydrolysis of the excess acid halide. Unfortunately, if these conditions were not observed it was found that the product yield was not particularly satisfactory. At least, this was the finding when attempts were made to carry out the reaction in the conventional way, using a sodium salt of a weak acid or sodium hydroxide as the acid-accepting agent.

In accordance with the present invention, it has been found that, for some reason, potash is particularly beneficial. It is not subject to limitations and conditions, which are found in the use of soda ash. There appears to be no particularly good explanation of this phenomenon and accordingly, the present invention is not intended to be limited to any particular theory of operation.

Use of potash as the neutralizing agent has a number of advantages. First and most noticeable, it causes a direct increase in the yield. Second and almost equally important, for some reason much less acid halide is required to carry out a successful reaction when potash is present. Instead of the large excesses formerly required, only a moderate excess is now found necessary. This advantage is particularly significant in the case of one of the alkoxy benzoyl chlorides, which are very susceptible to hydrolysis, and with this important class of acid chlorides our invention is particularly useful.

It is an important further advantage of the present method that the use of potash as contrasted with the prior use of soda ash makes the reaction surprisingly insensitive to the purity of this acid chloride, and/or its freedom from impurities normally inherent in its production, such as salicylic acid and thionyl chloride.

This is of very definite advantage. Using soda ash, acylation of a material such as 4,4'-diamino-stilbene-2,2'-disulfonic acid, with ortho-methoxy- and ortho-ethoxybenzoyl chloride, is found to be very seriously affected by small amounts of impurities, such as salicylic acid or its chloride. In the methods used in the art, presence of some salicylic acid or its chloride is almost inevitable. This is due to the fact, that in the alkylation of salicylic acid, the resulting alkyl ethers usually contain small amounts of salicylic acid, since the alkylation reaction is very difficult to force to completion.

In general, the process as carried out in accordance with the present invention, is quite simple. Direct reaction is readily carried out. It is preferable to keep the temperature below ordinary room temperature, in order to minimize side reac-

3 tions, but satisfactory results can be obtained at temperatures up to about 40° C. Furthermore, the precise proportions of potash is not particularly critical. A sufficient excess is used, so that the reaction medium is never permitted to become acidic. More than this amount has no particular benefit.

It has also been found that the use of potash, in accordance with the present invention, can be combined with the use of ketonic solvents, such as described in the copending application of Eberhart et al., Serial No. 24,107, filed April 28, 1948, now abandoned. When using both potash and a ketonic solvent in this manner, superior results are obtained to those which can be obtained by the use of either alone.

A highly suitable method of operation is to dissolve the amino stilbene sulfonic acid in an aqueous potash solution, to add thereto the ketonic solvent, if one is to be used; and then to add the aroyl halide. The latter is preferably added slowly, with continuous agitation. Temperature, as noted above, should be maintained below 40° C. In the case of the exemplary 4,4'-diamino-stilbene-2,2'-disulfonic acid, the desired acylation product separates from solution in excellent yield in the form of its di-potassium salt.

It has been found that the present invention may be applied with the halides of benzoic acid and its substitution products, such as the isomeric toluic acids, and their higher homologues, halobenzoic acids, nitrobenzoic acids, acylaminobenzoic acids, azodi- and azoxydi-benzoic acids, and cyanobenzoic acids. More than one substituent may be present. These substituents may be the same, as for example in dichlorobenzoic acids, or different as in nitrotoluic acids. It has been found that particularly advantageous results are obtained with alkoxybenzoic acids, such as anisic acid, salicylic acid methyl ether, ortho-ethoxybenzoic acid, 2,3-dimethoxybenzoic acid, and the like.

In carrying out the reaction, one factor may be noted. Amino stilbenes such as 4,4'-diamino-2,2'-disulfonic acid are not readily soluble in water per se. Their alkali metal salts, however, are quite soluble. It is not necessary to start the reaction with the potassium salt. For example, the acid may be added to water and dissolved by the addition of an equivalent amount of caustic soda or caustic potash. The novelty of the present invention lies in the use of potash, over and above the alkali required to dissolve the amino stilbene sulfonic acid, as an acid-accepting agent.

The present invention will be more fully illustrated in conjunction with the following examples. These examples are given solely by way of illustration. Except as otherwise noted, all parts are by weight and all temperature degrees centigrade.

Example 1

In order to illustrate a preferable procedure in accordance with the present invention, 16.7 parts of 4,4'-diamino-stilbene-2,2'-disulfonic acid is dissolved in 50 parts of water by the addition of an equivalent amount of caustic soda. Then 87.1 parts of potassium carbonate solution containing 27 parts by weight of anhydrous potassium carbonate, and 41.5 parts of acetone are added. The resultant solution is stirred and cooled to 8°-10° C. and maintained at this temperature while 22.7 parts of technical ortho-ethoxybenzoyl chloride are added dropwise over a period of about 15 minutes. As will be seen

4 from the resultant precipitation, reaction occurs largely during this interval. Stirring is maintained for an additional 15 minutes at 8°-10° C. and then for about 1½ hours at room temperature. The reacted mixture is diluted to volume of about 500 parts of water and stirred for an additional ½ hour. Isolation of the product is obtained by filtering out the precipitate, washing the latter with 2% potassium carbonate solution, and then with a small amount of water. Finally, drying is carried out at 105° C. An excellent yield of good quality product is obtained.

Example 2

15 Example 1 was repeated. However, in order to show the superiority of the use of potassium carbonate, in this experiment, sodium carbonate solution (20% solution for addition of the acid binder and 2% solution for washing purposes) was substituted for the potassium carbonate solution. Additional amounts were added intermittently during acylation, as were required in order to keep the slurry alkaline. The resultant weight yield is slightly less than half the yield obtained in Example 1.

Example 3

30 4,4'-diaminostilbene-2,2'-disulfonic acid, 16.7 parts, is added to 50 parts of water, 7.5 parts of 50% sodium hydroxide, and 80 parts of 20% potassium carbonate solution, and cooled to 8°-10° C. There is then added gradually 22.7 parts of o-ethoxybenzoyl chloride, stirring being continued one and one-half hours after the addition is complete. The reaction mixture is then diluted to the volume of 500 parts of water and filtered. The product is washed with 2% potassium carbonate solution, and is obtained in excellent yield and good quality.

Example 4

40 Example 3 was performed, using sodium carbonate instead of potassium carbonate. The resulting weight yield was reduced by more than half.

Example 5

50 12.6 parts of 4,4'-diaminostilbene-2,2'-disulfonic acid is dissolved in 86 parts of water containing 5.9 parts of 50% sodium hydroxide solution, 53 parts of acetone, and a solution of 17.9 parts of potassium carbonate in 30 parts of water. This is cooled to 10° and gradually treated with 15 parts of o-anisoyl chloride. When acylation is complete, the reaction mixture is diluted and filtered. An excellent yield of the acylated product is obtained.

Example 6

60 Example 5 is performed in the same way, using sodium carbonate instead of potassium carbonate. The yield of product is very substantially inferior.

Example 7

75 To a solution resulting from mixing at 20° C. 16.7 parts by weight of 4,4'-diamino-stilbene-2,2'-disulfonic acid, 7.5 parts of 50% caustic soda solution and 87.1 parts of potassium carbonate, is slowly added with stirring, a solution of 19.3 parts of p-nitrobenzoyl chloride dissolved in 31.6 parts of acetone. The experiment is continued as in Example 1, except that 39 parts of additional potassium carbonate solution is added to maintain alkalinity. The product is obtained in substantially quantitative yield.

Example 8

Example 7 was repeated, substituting sodium carbonate for the potassium carbonate. A much lower yield of the product is obtained.

I claim:

1. In a process of reacting, in aqueous medium, 4,4'-diamino-stilbene-2,2'-disulfonic acid with a carboxylic acid chloride of the benzene series, whereby hydrochloric acid is liberated, the improvement which comprises carrying out the reaction at a temperature of from -5° C. to 40° C. in the presence of potassium carbonate to act as acid binder for the liberated hydrochloric acid.

2. A process according to claim 1 in which the aqueous medium contains acetone.

3. A process according to claim 1 in which the carboxylic acid chloride is substituted by an alkoxy group.

4. A process according to claim 1 in which the carboxylic acid chloride is o-ethoxybenzoyl chloride.

5. A process according to claim 1 in which the carboxylic acid chloride is p-methoxybenzoyl chloride.

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