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PROCESS FOR PREPARING ESTERS OF PYRIDINE THIONES

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5 Claims. (Cl. 260—294.8)

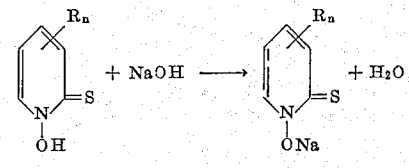
This invention relates to a process for the preparation of esters of pyridinethione derivatives. More particularly, this invention relates to a method in which the sodium salt of a 1-hydroxy-2-pyridinethione compound is reacted with a fatty acid anhydride to form in high yields the corresponding fatty acid ester.

The yield of the esters formed by the novel method of this invention is from 80 to 90 percent or more as compared to about 35 percent for methods known in the art for preparing these same compounds. Another advantage of this process is that it is carried out at temperatures ranging from about —5° C. to about +30° C. thus avoiding the formation of undesirable side products which takes place at the temperatures utilized in the prior art processes, i.e. 80°–90° C. Thus a purer product is obtained with the method of this invention than with prior art methods since the reaction emperature is substantially decreased. The purity of the products of this invention is shown by the sharp melting points as well as by the infrared spectra exhibited by these materials. Therefore, the products produced by the process of this invention require no recrystallization, while the same products, prepared by known methods, must be recrystallized for comparable purity.

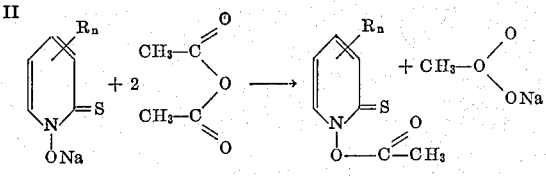
In the process of this invention there is first prepared the sodium salt of a 1-hydroxy-2-pyridinethione compound by reacting sodium hydroxide with the pyridinethione compound and then in a second step reacting sodium salt with a fatty acid anhydride under aqueous conditions. The potassium and lithium salts of the pyridinethione starting materials are also useful.

The two-stage process of the present invention proceeds according to the equations below where, for purposes of illustration, acetic acid anhydride is shown as the fatty acid anhydride:

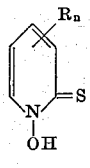
I



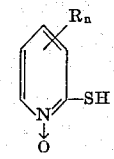
II



In the Equation I above the compound:



may be in tautomeric equilibrium with the compound:



wherein R is hydrogen, alkyl of not more than 5 carbon atoms, alkoxy of not more than 5 carbon atoms or a halogen selected from the group consisting of chlorine, bromine and iodine and *n* is a positive interger of no greater than four and preferably one.

Useful 1-hydroxy-2-pyridinethione compounds include, for example, 1-hydroxy-2-pyridinethione, 1-hydroxy-3-methoxy-2-pyridinethione, 1-hydroxy-5-butoxy-2-pyridinethione, 1-hydroxy-3-methyl-2-pyridinethione, 1-hydroxy-4,6-di-n-butyl-2-pyridinethione, 1-hydroxy-3,4-dichloro-2-pyridinethione, 1-hydroxy-5-bromo-2-pyridinethione.

Suitable fatty acids whose anhydrides are utilizable as starting materials in the process of this invention include: acetic, n-propionic, isopropionic, n-butyric, isobutyric, acrylic, crotonic and sorbic. Any fatty acid anhydride yielding a water-soluble fatty acid is suitable for the process of this invention.

Although the stoichiometric quantity of fatty acid anhydride can be employed in this invention, preferably from about 3 to about 10 moles of acetic anhydride are employed per mole of the sodium salt of the 1-hydroxy-2-pyridinethione compound charged to the reactor. Generally, the temperature will range from about —5° C. to about +30° C. and preferably will be from about 0° C. to about 15° C. If less than about 3 moles of anhydride per mole of the pyridinethione compound are untilized, it has been found that a lower yield of a product exhibiting a lower melting point than the preferred product is obtained. In the process of this invention the preferred pressure is atmospheric although pressures ranging from subatmospheric up to 10 atmospheres or more can be used. The reaction time will vary from about 0.1 to 3 hours or more depending upon the particular reactants and reaction conditions utilized.

Recovery of the products of this invention, which are insoluble in the reaction medium employed, can be accomplished by filtration, centrifugation, decantation, etc.

The following examples which illustrate the process of this invention are to be considered not limitative.

EXAMPLE I

(A) Preparation of the sodium salt of 1-hydroxy-2-pyridinethione:

A solution of the sodium salt of 1-hydroxy-2-pyridinethione was prepared by neutralizing an aqueous slurry of 1-hydroxy-2-pyridinethione with 25 percent aqueous sodium hydroxide until the pH of the resulting solution was in the range of 6.5 to 7.0, the sodium salt concentration was 12.5 weight percent.

(B) Preparation of the acetate of 1-hydroxy-2-pyridinethione:

Five hundred grams of this solution (63 g. of the sodium salt of 1-hydroxy-2-pyridinethione, 0.422 mole) was diluted with 500 grams of water and the solution then cooled to 0–5° C. To the cold solution, 125 g. acetic anhydride (1.23 moles) were added and the mixture stirred at 0° to 5° C. for 0.5 hour. The yellow product precipitate was then filtered out, washed several times with cold water, and dried for 16 hours in a vacuum oven at 50° C. The dried product (the acetate of 1-hydroxy-2-pyridinethione) weighed 64.3 grams (0.380 mole); M.P. 88°–88.5° C. Yield was 90.2 percent of the theoretical quantity.

The product was analyzed for carbon, hydrogen and sulfur and the following results were obtained:

Analysis.—Calc'd for $C_7H_7O_2NS$: C, 49.70; H, 4.14; S, 19.95. Found: C, 49.59; H, 4.43; S, 19.10.

EXAMPLE II

Two hundred grams of an aqueous solution of the sodium salt of 1-hydroxy-2-pyridinethione (0.097 mole) was diluted with 400 grams of water and the solution cooled to 0° C. To the cold solution 35 mls. (0.343 mole) of acetic anhydride was added and the mixture stirred at 0° to 5° C. for 0.5 hour. The yellow product, which had precipitated from the reaction mixture, was then recovered by filtration, washed several times with cold water and dried for 16 hours in a vacuum oven at about 50° C. The dried product (the acetate of 1-hydroxy-2-pyridinethione) weighed 0.075 mole which corresponds to a yield of 77.8 percent.

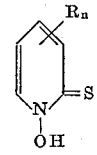
The product was submitted for infrared analysis and was shown to be pure 1-hydroxy-2-pyridinethione acetate.

The esters of this invention are active bactericides and fungicides. The fatty acid derivatives of this invention can, therefore, be used as preservatives (for example, in leather, paper and fabrics) and especially in paints and varnish to render them resistant against mildew or other fungus attack. In the protection of paints, for example, the mixed anhydrides are simply mixed with the paint.

The mixed anhydrides of this invention find further use as agricultural fungicides, the mixed anhydride being added either directly to the soil (by sprinkling the mixed anhydride itself or a composition of the mixed anhydride and suitable diluents onto the surface of the soil and then thoroughly intermixing the soil and mixed anhydride) or directly to plant foliage by spraying a composition thereof with a suitable carrier.

What is claimed is:

1. A process for the preparation of an ester which comprises (A) neutralizing an aqueous slurry of a compound of the formula:

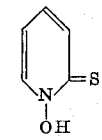


wherein R is selected from the group consisting of hydrogen, alkyl of not more than 5 carbon atoms, alkoxy of not more than 5 carbon atoms, and a halogen selected from the group consisting of chlorine, bromine and iodine,, and *n* is an integer no higher than four, with sodium hydroxide until the pH of the resulting solution is in the range of about 6.5 to 7 whereby the sodium salt of the said compound is formed and (B) reacting the said sodium salt in aqueous solution with from about 3 to about 10 moles of an anhydride of a fatty acid selected from the group consisting of acetic, n-propionic, isopropionic, n-butyric, isobutyric, acrylic, crotonic and sorbic acid.

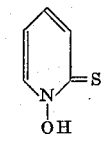
2. The process of claim **1** wherein the temperature of the reaction is from about −5° C. to about +30° C.

3. The process of claim **1** wherein the said anhydride is acetic anhydride.

4. The process of claim **1** wherein the said compound is:



5. The process of claim **1** wherein the said anhydride is acetic anhydride, the said compound is:



and the temperature of the reaction is from about −5° C. to about +30° C.

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