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PREPARATION OF OLEFINIC NITRILES BY DEHYDRATION WITH ACETIC ANHYDRIDE

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3 Claims. (Cl. 260—464)

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This application relates to the dehydration of α-hydroxy acid derivatives especially amides or ammonium salts thereof with acetic anhydride to give unsaturated compounds.

The preparation of unsaturated compounds using α-hydroxy acid derivatives initially is shown in U. S. Patents Nos. 2,183,357 and 2,265,814 of Ritchie et al. In the procedure described in those patents the α-hydroxy compounds such as mono- or dialkyl-glycollic acid derivatives are first acetylated, and this acetylated material is converted to an unsaturated compound. My invention constitutes an improvement over the procedure described in the Ritchie patents in that there are several features of my process which are absent in the procedure disclosed in those patents.

One object of my invention is to provide a one-step process of preparing unsaturated compounds directly from derivatives of α-hydroxy aliphatic acids. Another object of my invention is to provide a process of making unsaturated compounds in which crude materials may be employed. A further object of my invention is to provide a process of making unsaturated compounds from glycollic acid derivatives having high yields. Other objects of my invention will appear herein.

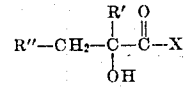
Whereas in the processes of the Ritchie patents a plurality of steps are involved, refined materials are necessary for use and the yields are not too good, based on the glycollic acid derivatives employed initially, in the procedure in accordance with my invention the process is carried out in one step without any intermediate reaction being necessary, the yields of unsaturated compounds are high based on the glycollic acid derivatives used and it is not necessary to refine the glycollic acid derivatives which are employed as the starting materials.

I have found that by the pyrolysis of a solution in acetic anhydride of certain derivatives of glycollic acids, α,β-unsaturated compounds are obtained with but small formation of low boilers and undesirable gaseous products and also high yields are obtained and the by-products of the reaction may be recycled to obtain almost complete conversion. I have found that in the presence of excess acetic anhydride, amides, esters, nitriles, or ammonium salts or mixtures thereof of the mono- or dialkyl glycollic acids may be dehydrated in the vapor phase to give the corresponding α,β-unsaturated compounds.

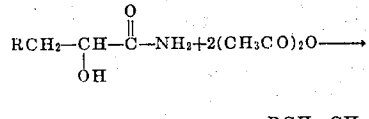
According to the present invention, lower alkyl esters or nitriles of α,β-unsaturated monocarboxylic aliphatic acids are produced by the vapor

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phase decomposition of the acetic anhydride solution of esters, amides, nitriles or ammonium salts of the mono- and dialkyl glycollic acids. The compounds which are suitable for use as the starting material of my invention may be illustrated by the formula:



in which R′ and R″ are hydrogen or alkyl and X is either alkoxy, NH_2 or ONH_4. The following equation illustrates the reaction which takes place according to my invention employing the amide of a dialkyl glycollic acid as the starting material.



$$RCH=CH-C\equiv N+4CH_3COOH$$

In carrying out my invention, atmospheric pressures are permissible and ordinarily will be employed. The optimum temperature of the reaction may be varied in accordance with the wishes of the individual operator. In general, however, it is preferred to use temperatures ranging between 400 and 600° C. in carrying out the pyrolysis process. The pyrolysis is conveniently carried out by passing the vapors of the acetic anhydride solution of the glycollic acid derivative through a heated tube together with an inert diluent gas such as nitrogen or carbon dioxide. The tube may be suitably packed with quartz, pyrex chips or carbon rods or inert material to increase the effective heating surface.

The derivatives which may be used can be prepared by passing anhydrous ammonia through a concentrated solution of the acid or by ammonolysis of one of the lower alkyl esters of the acid. In the case of lactic acid the concentration may be effected by prolonged heating at 140°–150° C. or by azeotropic distillation of the H_2O present. Xylene and toluene are typical of the solvents which may be used to effect removal of the water. The solvent is then decanted and the concentrated acid treated with anhydrous ammonia at elevated temperature such as 140 to 160° C. This gives a mixture high in amide content.

Instead of the amide or the mixture of amide and ammonium salt, one may employ the alkyl ester of the glycollic acid such as obtained by esterifying the acid with a lower aliphatic alcohol using sulfuric acid catalyst at an elevated

temperature. If desired, the nitrile of an α-hydroxy aliphatic acid may be employed as the starting material such as, for example, α-hydroxy isobutyronitrile. Some of the compounds which may be employed as the starting material of my process are the following: methyl lactate, ethyl lactate, α-hydroxymethylisobutyrate, lactic amide, ammonium lactate, lactic amide-ammonium lactate mixture, α-hydroxyisobutyronitrile, N-acetyl-α-hydroxyisobutyramide, methyl-α-hydroxy isobutyrate, or, as a matter of fact, any of the lower molecular weight compounds such as have no more than 8 carbon atoms in a straight chain, which correspond to the formula given herein. The pyrolysis process may be carried out by passing a current of the vapor through a tube such as described in the Ritchie patents. These patents may be referred to for any details which are not provided for in my description of my process which is an improvement over the process described by the Ritchie patents. The following examples illustrate my invention:

Example 1

90 grams of lactic amide were dissolved in 102 grams of hot acetic anhydride. This solution was dropped slowly through a preheater at 140 to 150° C. and then through a tube packed with pyrex rings at 550° C. The contact time was 6 seconds. Distillation of the material obtained gave 15 grams of acrylonitrile boiling at 76° C. at 735 mm. pressure. Some acetaldehyde was also formed.

Example 2

100 grams of a mixture of lactic amide and ammonium lactates were dissolved in 100 grams of hot acetic anhydride. This material was passed through a preheater at 140 to 150° C. The material was then passed through a pyrolysis tube filled with pyrex chips, the temperature of the tube being maintained at 475 to 525° C. A flow of nitrogen at the rate of 1 to 2 cubic feet per hour was also passed through to conduct the material therethrough. The contact time was 5 seconds. Distillation gave no low boilers but 20 grams of acrylonitrile were obtained. This material boiled at 74–78° C. at 735 mm. pressure. The residue was repassed through the pyrolysis tube using a six-seconds contact time and 18 grams further of the nitrile were obtained. The total yield was 38 grams or 73%.

Example 3

90 grams of lactic amide were dissolved in 300 grams of hot acetic anhydride. The material was preheated at 140 to 150° C. and then passed through a chamber packed with pyrex rings at 550° C. using a four-second contact time. Nitrogen was also passed at the rate of 1 to 2 cubic feet per hour. Distillation gave 24 grams of acrylonitrile which boiled at 75–77° C. at 735 mm. pressure.

Example 4

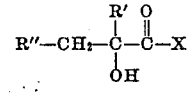
200 grams of methyl lactate was dissolved in 300 grams of acetic anhydride and the solution was passed through a preheater packed with pyrex chips at 125 to 150° C. The solution was then pyrolyzed at 550° C. by passing through a pyrolysis tube filled with pyrex rings. A current of nitrogen was passed through to carry the material through the tube at the rate of 2 cubic feet per hour. The contact time was 6 seconds. Distillation gave 25 grams of methyl acrylate.

Example 5

100 grams of methyl lactate was dissolved in 250 grams of acetic anhydride and the solution was preheated at 150° C. and then pyrolyzed at 550° C. using a 6 second contact time. The nitrogen flow was 2 cubic feet per hour. Distillation gave 40 grams of methyl acrylate.

I claim:

1. A method for producing an α,β-unsaturated nitrile which comprises pyrolyzing in the absence of a catalyst an acetic anhydride solution of a compound having the following formula:



R′ and R″ being substituents selected from the group consisting of hydrogen and alkyl and X being a radical selected from the group consisting of NH_2 and ONH_4.

2. A method for producing an α,β-unsaturated nitrile which comprises pyrolyzing in the absence of a catalyst an acetic anhydride solution of lactic amide.

3. A method for producing an α,β-unsaturated nitrile which comprises pyrolyzing in the absence of a catalyst an acetic anhydride solution of ammonium lactate.

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