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PROCESS FOR THE PRODUCTION OF UNSATURATED ACIDS AND ESTERS

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2 Claims. (Cl. 260—486)

The present invention relates to a process for the production of unsaturated acids, especially alpha,beta-unsaturated acids, and their esters, and, more particularly, to a process for the production of acrylic acid and esters thereof.

Heretofore, unsaturated acids were obtained from the corresponding unsaturated aldehydes only with difficulty and considerable expense. This was due to the fact that most oxidizing agents attacked the double bond in the unsaturated aldehyde at the same time that they oxidized the aldehyde to an acid. The aforesaid action caused the production of many undesirable reaction products, including polymers. Thus, when unsaturated aldehydes, like acrolein, were directly oxidized, a very dense reaction product was obtained, accompanied by strong polymerization phenomena, and the desired unsaturated acids occurred only in very small amounts. For this reason special oxidizing agents, such as silver oxide, had to be used if direct oxidation was to be effective in any measure at all. For example, although it was possible to obtain acrylic acid by direct oxidation of acrolein, or even of allyl alcohol, the reaction was unsatisfactory in yield and necessarily very costly by reason of the fact that silver oxide had to be employed. The art developed a somewhat cheaper and more convenient method of producing these unsaturated acids by halogenating the corresponding unsaturated alcohols, thereafter oxidizing to form the halogenated acid, and finally removing the halogen to form the unsaturated acid. Thus, for some time, acrylic acid was produced as those skilled in the art know by brominating allyl alcohol, oxidizing, and adding zinc to split off the bromine, but this too proved far from satisfactory in yield. Other complicated methods have been attempted, but none, so far as I am aware, has been economically and commercially successful in producing these unsaturated acids from aldehydes or from beta-alkoxycarboxylic acids.

It is an object of the present invention to produce unsaturated acids cheaply and conveniently from unsaturated aldehydes without the use of expensive oxidizing agents.

It is another object of the invention to produce unsaturated acids easily and economically from unsaturated aldehydes substantially without the formation of polymers or other undesirable reaction products.

A further object of the invention is to produce alpha,beta-unsaturated acids and esters from unsaturated aldehydes by a process wherein oxygen gas may be used as the oxidizing agent with substantially no formation of polymers or other undesirable products.

My invention also has for its object the production of alpha, beta-unsaturated acids and their esters by heating beta-alkoxycarboxylic acids with an acidic substance.

It is also within the contemplation of the invention to produce acrylic acid from acrolein by a simple and inexpensive method.

My invention also contemplates the production of acrylic acid and esters thereof by treating beta-alkoxypropionic acids with an acid catalyst at elevated temperatures.

Furthermore, the present invention also provides a process of producing acrylic acid and the ethyl ester of acrylic acid by treating beta-ethoxy-propionic acid with an acidic agent at elevated temperatures.

Other objects and advantages of my invention will become apparent from the following description of a preferred procedure for carrying it into practice.

Broadly stated, in carrying the present invention into practice, unsaturated acids are produced from unsaturated aldehydes by reacting unsaturated aldehydes with alcohols to form beta-alkoxyaldehydes, oxidizing these beta-alkoxyaldehydes to beta-alkoxycarboxylic acids, and splitting off alcohol from the thus-formed beta-alkoxycarboxylic acids to leave a double bond. In this three step process, I prefer to produce the beta-alkoxyaldehydes by the process disclosed in my co-pending application, Ser. No. 272,850, entitled "Process for the production of beta-alkoxyaldehydes," filed May 10, 1939. I also prefer to produce the beta-alkoxycarboxylic acids from the beta-alkoxyaldehydes by the process disclosed in my co-pending application, Ser. No. 272,851, entitled "Process for the production of beta-alkoxycarboxylic acids," filed May 10, 1939. Unsaturated acids and their esters are produced from beta-alkoxycarboxylic acids and their esters by subjecting them to elevated temperatures in the presence of an acidic substance as a catalyst. For example, beta-alkoxycarboxylic acids produced in accordance with the process disclosed in my co-pending application may be heated in the liquid phase with mineral acids, halogenated fatty acids, or aromatic sulfonic acids, all of which have given good results. Thus, sulfuric acid, monochloroacetic acid, phosphoric acid, benzol-sulfonic acid and toluolsulfonic acid have been most successfully employed. Under these conditions, the beta-substituted alkoxy group is split off with the corresponding formation of a double bond in the

alpha-beta position. The molecule of alcohol which is split off upon the formation of this olefinic double bond may be used to esterify the free carboxy group, if desired, by prolonging the exposure of the solution to the action of heat and the acidic substance. This esterification can also be facilitated by carrying out the acid-heat treatment in the presence of excess alcohol, whereby the ester of the corresponding unsaturated acid is obtained directly.

It has been found that the presence of a small amount of a strong reducing agent is of substantial aid in completely avoiding the formation of polymerization products. For this reason, I have found it advantageous to add about 1 to about 2% of hydroquinone, or quinol, to the mixture.

Within the contemplation of the present invention, any beta-alkoxycarboxylic acid or any ester of beta-alkoxycarboxylic acids may be employed. These include, for example, beta-alkoxypropionic acid, beta-methoxypropionic acid ester, beta-ethoxybutyric acid and its esters, beta-ethoxy-alpha-methylpropionic acid, beta-ethoxybutyric acid, beta-ethoxyvaleric acid, beta-ethoxyhydrocinnamic acid and the like.

In accordance with the general principles of my invention, acrolein is reacted with ethyl alcohol to form beta-ethoxypropionaldehyde. The beta-ethoxypropionaldehyde is then oxidized to beta-ethoxypropionic acid. The thus-formed beta-ethoxypropionic acid is heated with toluol sulfonic acid, whereby acrylic acid and its ethyl ester are formed, substantially free of the presence of polymers and others undesirable reaction products. If this latter reaction is carried out in a distillation vessel, the acrylic acid and the ethyl ester thereof formed during the reaction can be distilled off as they are formed. Another method of recovery is first to heat the reaction mixture under reflux and, if desired, under pressure, until the reaction has proceeded sufficiently far, and thereafter to work up the reaction product obtained by distillation. Such distillation may be under reduced pressure, if desired.

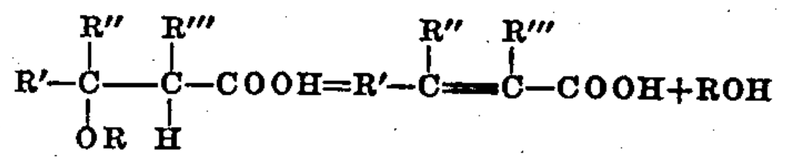
In a further modification of my invention, the splitting-off of the ethoxy group may be carried out in the vapor or gas phase. This is accomplished by conducting the beta-alkoxycarboxylic acids over acidic substances impregnated upon carriers. It has been found that successful results are obtained by using such acidic substances as aluminum metaphosphate, silicic acid, phosphoric acid, sulfuric acid and the like, and these are impregnated upon such carriers as clay, active carbon, tungstic acid or the like. This gas phase reaction may be carried out at ordinary, elevated or reduced pressures.

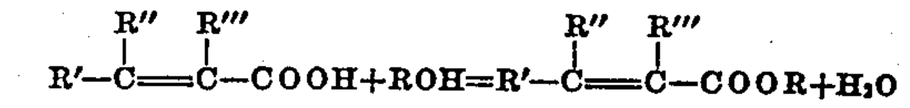
For the purpose of giving those skilled in the art a better understanding of carrying my invention into practice, the following illustrative example is given:

Example

In accordance with the examples given in my co-pending applications, cited supra, acrolein is used as a starting material and reacted with ethyl alcohol in the presence of water and an acid catalyst, whereby beta-ethoxypropionaldehyde is formed. This is transformed into beta-ethoxypropionic acid by oxidation with molecular oxygen. About 118 grams of the thus-formed beta-ethoxypropionic acid is heated at about atmospheric pressure with about 5 grams of toluolsulfonic acid and about 1 to about 2 grams of hydroquinone. Heat is applied until distillation products are formed, and at temperatures of about 110° C. to about 140° C., a liquid mixture is distilled off. This consists essentially of acrylic acid and acrylic acid ethyl ester, together with a little ethoxypropionic acid ethyl ester and unreacted beta-ethoxypropionic acid. The water formed by the esterification of the acid with the split-off alcohol will also be present. Using a small rectification column, these reaction products are satisfactorily separated from each other, and simultaneously the still unreacted beta-ethoxypropionic acid is subjected to an extensive splitting-off of the ethoxy group.

Although my invention has been described in connection with a preferred embodiment, it will be observed that variations may be resorted to and are within the purview of the appended claims. In the foregoing illustrative example, the production of acrylic acid and of acrylic acid ethyl ester was described. Of course, other apha-beta unsaturated acids and esters can be produced by the following reaction and will have the following structural formulae:





wherein R is an alkyl group and R', R'' and R''' are hydrogen atoms or organic radicals.

I claim:

1. A process for producing a mixture of acrylic acid and ethyl ester of acrylic acid which comprises mixing about 118 parts of beta-ethoxy propionic acid, about 5 parts of toluol sulfonic acid and about 1 to 2 parts of hydroquinone to form a liquid mixture, and heating said mixture to a temperature not appreciably higher than the boiling point of acrylic acid until acrylic acid and ethyl ester of acrylic acid are formed.

2. A process for producing a mixture of unsaturated acids and esters thereof from beta-alkoxy monocarboxylic acids which comprises heating a mixture of beta-alkoxy monocarboxylic acid selected from the group consisting of beta-ethoxy propionic acid, beta-ethoxy butyric acid, beta-ethoxy valeric acid, and beta-ethoxy alpha-methyl propionic acid a small amount of a reducing agent, and an acidic catalyst selected from the group consisting of benzol sulfonic acid and toluol sulfonic acid in catalytic amount, in a liquid phase to the boiling point of the mixture to form an unsaturated acid and the alkoxy group so split off combines with a portion of the unsaturated acid to form an ester thereof, and distilling off said unsaturated acid and said ester thereof to obtain a distillate containing the said unsaturated monocarboxylic acid and said ester thereof.

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