Patented May 22, 1945 2,376,704

UNITED STATES PATENT OFFICE

2,376,704

PREPARATION OF ESTERS OF ALPHA-BETA UNSATURATED MONOCARBOXYLIC ACIDS

Frederick E. Kung, Akron, Ohio, assignor to The B. F. Goodrich Company, New York, N. Y., a corporation of New York

No Drawing. Application October 1, 1943, Serial No. 504,602

6 Claims. (Cl. 260—486)

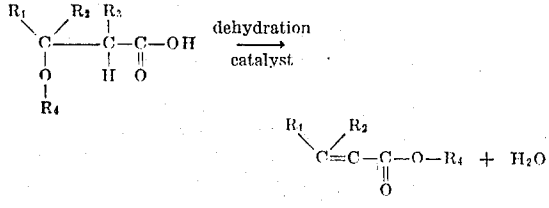
This invention relates to a novel process for the preparation of esters of alpha-beta unsaturated monocarboxylic acids, particularly to the preparation of alkyl esters of alpha-beta unsaturated monocarboxylic acids such as methyl acrylate.

In my copending application Serial No. 393,671, filed May 15, 1941, an economical method of preparing lactones of beta-hydroxy monocarboxylic acids by the reaction of a ketene with a carbonyl compound such as an aldehyde or ketone has been described. The ease with which such lactones are now obtained makes it desirable to use these compounds as starting materials for the synthesis of other compounds including the alpha-beta unsaturated monocarboxylic acid esters, such as the alkyl acrylates and methacrylates, which are extremely useful as polymerizable materials in the production of synthetic resins, synthetic rubber and the like.

It has also been disclosed in my copending application Serial No. 405,512, of which this application is a continuation-in-part, that the above-described lactones react with monohydric alkyl alcohols to form good yields of beta-alkoxy monocarboxylic acids.

The invention of this application has for its object the conversion of such beta-alkoxy monocarboxylic acids into alkyl esters of alpha-beta unsaturated monocarboxylic acids. Another object of the invention is to convert lactones of beta-hydroxy monocarboxylic acids into such alkyl esters by a single-step reaction without the necessity of first preparing a beta-alkoxy acid.

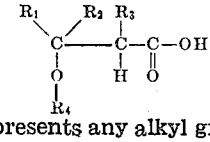
These objects are accomplished by the discovery that beta-alkoxy monocarboxylic acids yield alkyl esters of alpha-beta unsaturated monocarboxylic acids on treatment with a dehydration catalyst. The reaction proceeds as indicated by the following equation:



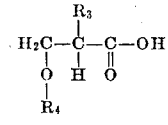
where R_1, R_2 and R_3 represent hydrogen or hydrocarbon groups and R_4 represents an alkyl group.

It is quite surprising that acids of this type yield esters on dehydration since ordinarily the dehydration of monocarboxylic acids yields acid anhydrides.

As indicated by the above equation any beta-alkoxy monocarboxylic acid having at least one hydrogen atom connected to the alpha-carbon atom may be employed. Examples of such beta-alkoxy monocarboxylic acids include the beta-methoxy, beta-ethoxy, beta-propoxy, beta-isobutoxy, beta-octoxy and beta-lauroxy derivatives of propionic acid, which yield alkyl esters of acrylic acid on dehydration; similar alkoxy derivatives of alpha-methyl propionic acid (isobutyric acid), which yield alkyl esters of methacrylic acid on dehydration, and various other beta-alkoxy aids of the formula



wherein R_4 represents any alkyl group, preferably an alkyl group of less than ten carbon atoms, and R_1, R_2 and R_3 represent either hydrogen atoms; alkyl groups such as methyl, ethyl, butyl, etc.; cycloalkyl groups such as cyclohexyl; aryl groups such as phenyl and aralkyl groups such as benzyl; or other hydrocarbon groups. Preferably low-molecular weight aliphatic beta-alkoxy monocarboxylic acids containing from about 4 to 12 carbon atoms are employed, acids of the formula



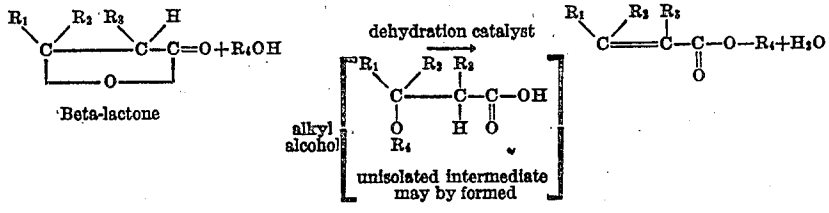
wherein R_4 is a lower alkyl group and R_3 is hydrogen or a lower alkyl group, which acids yield alkyl esters of acrylic and alpha-alkyl acrylic acids on dehydration, being particularly preferred. All these acids may be prepared by the reaction of beta-lactones with alkyl alcohols, in the manner described in my copending application Serial No. 405,512, or by any other known method.

Treatment of the beta-alkoxy acid with a dehydration catalyst may be effected in various ways and at varying temperatures and pressures depending on the particular compound being dehydrated. For example, the alkoxy acid may be heated with and distilled at normal or reduced pressures from a dehydration catalyst of the strong acid type such as sulfuric acid, phosphoric acid, methane sulfonic acid, benzene sulfonic acid, toluene sulfonic acid or the like or

the alkoxy acid may be passed in the vapor phase at elevated temperatures of about 200 to 400° C. over a surface active dehydration catalyst such as silica gel, activated alumina, aluminum phosphate and the like. The amount of the catalyst employed may be varied from a very small amount in some cases to stoichiometrical proportions in other cases. Other methods of dehydrating organic compounds by the use of these and other well-known dehydration catalysts are well known to the art and may, in general, be applied to the dehydrations herein described.

When carrying out the dehydration it is desirable, especially if a polymerizable ester of an alpha-beta unsaturated monocarboxylic acid such as an acrylic ester is obtained as the product, that a substance be present which prevents the polymerization of the ester formed. Suitable substances for this purpose include copper, copper salts, hydroquinone, catechol, phenyl-beta-naphthylamine and other well-known polymerization inhibitors.

As mentioned hereinabove, instead of employing a beta-alkoxy monocarboxylic acid of the type described, it is also possible, in accordance with this invention, to employ in the dehydration process a mixture of a lactone of a beta-hydroxy monocarboxylic acid having at least one hydrogen atom on the alpha carbon atom, and an alkyl alcohol. While, as disclosed in my copending application Serial No. 405,512 referred to hereinabove, these materials react under ordinary conditions to form a beta-alkoxy monocarboxylic acid, in the presence of a dehydration catalyst, the reaction yields an ester of an alpha-beta unsaturated monocarboxylic acid, the beta-alkoxy acid being only an unisolated intermediate, if formed at all, in the process. This reaction may be formulated as follows:



wherein R_1, R_2, and R_3 represent hydrogen or hydrocarbon groups and R_4 represents an alkyl radical.

Thus, for example, beta-hydroxy propionic acid lactone together with an equivalent weight or an excess of an alkyl alcohol such as methanol or ethanol, may be refluxed in the presence of a dehydration catalyst such as sulfuric acid or toluene sulfonic acid and the mixture then distilled to produce good yields of an alkyl ester of acrylic acid. Other lactones of the above general formula, which may be prepared by the reaction of ketenes with aldehydes or ketones in the manner described in my copending application Serial No. 393,671, may also similarly be mixed with alkyl alcohols and then treated with a dehydration catalyst to produce alkyl esters of alpha-beta unsaturated monocarboxylic acids.

The following examples will illustrate the practice of the invention, the first two examples pertaining to the production of esters of alpha-beta unsaturated acids by the dehydration of beta-alkoxy monocarboxylic acids; and the third example pertaining to a single-step process for producing such esters directly from beta-lactones and alkyl alcohols.

Example I

26 parts of beta-methoxy propionic acid are heated in a distilling flask with 35 parts of concentrated sulfuric acid and a fraction of a part of copper acetate. The temperature of the reaction mass is maintained at about 200° C. for a half hour and distillation of the product is then effected. The distillate is a mixture of methyl acrylate and water which is purified by drying and redistillation. 13.5 parts of methyl acrylate (B. P. 67–72° C.) are thus obtained.

Example II

In one hour 34 parts of beta-methoxy propionic acid are passed into 10 parts of methane sulfonic acid and a fraction of a part of copper acetate at a temperature of 180–200° C. The product is then distilled and produces a 67% yield of methyl acrylate.

Example III

A mixture containing 72 parts of the lactone of beta-hydroxy propionic acid, 50 parts of absolute ethanol, 1 part of hydroquinone and 2 parts of sulfuric acid is refluxed in a distillation flask while 25 parts of sulfuric acid and 50 parts of ethanol are slowly added thereto. After about two hours the mixture is then distilled. Purification of the product produces 42 parts (49%) of pure ethyl acrylate.

I claim:

1. The method of preparing an alkyl ester of an alpha-beta unsaturated monocarboxylic acid which comprises heating a lactone of a beta-hydroxy monocarboxylic acid having at least one hydrogen atom on the alpha carbon atom with an alkyl alcohol in the presence of a dehydration catalyst and then distilling the product.

2. The method of preparing an alkyl ester of acrylic acid which comprises refluxing the lactone of beta-hydroxy propionic acid with an alkyl alcohol in the presence of sulfuric acid and then distilling the product.

3. The method of preparing ethyl acrylate which comprises heating beta-hydroxy propionic acid lactone and ethanol in the presence of a dehydrating acid catalyst and then distilling the product.

4. The method of preparing ethyl acrylate which comprises heating beta-hydroxy propionic acid lactone and ethanol in the presence of methane sulfonic acid and then distilling the product.

5. The method of preparing an alkyl ester of acrylic acid which comprises heating beta-hydroxy propionic acid lactone and an alkyl alcohol in the presence of methane sulfonic acid and then distilling the product.

6. The method of preparing an alkyl ester of an alpha-beta unsaturated monocarboxylic acid which comprises heating a lactone of a beta-hydroxy monocarboxylic acid having at least one hydrogen atom on the alpha carbon atom with an alkyl alcohol in the presence of methane sulfonic acid and then distilling the product.

FREDERICK E. KUNG.