Patented July 31, 1951

2,562,849

UNITED STATES PATENT OFFICE

2,562,849

PREPARATION OF ESTERS OF ALPHA,BETA-OLEFINIC CARBOXYLIC ACIDS

Richard R. Whetstone, Orinda, William J. Raab, Berkeley, and Seaver A. Ballard, Orinda, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

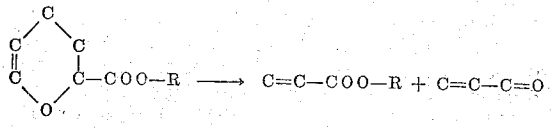
No Drawing. Application July 1, 1949, Serial No. 102,722

12 Claims. (Cl. 260—486)

1

This invention relates to a process for the preparation of esters of unsaturated carboxylic acids, and it more particularly relates to a process for the preparation of esters of alpha,beta-olefinic carboxylic acids, preferably the esters with beta,gamma-olefinic alcohols, by pyrolysis of certain dihydropyran compounds. In a more limited and preferred aspect, this invention is directed particularly to an improved process for the preparation of allyl acrylate and of esters of lower alpha-alkyl acrylic acids with lower beta-alkyl allyl alcohols, such as methallyl methacrylate, by controlled pyrolysis of dihydropyran carboxylic acid compounds.

In accordance with the present invention, esters of open-chain or aliphatic alpha,beta-olefinic carboxylic acids are prepared by controlled pyrolysis of Δ^5-dihydropyran-2-carboxylic acid compounds to effect their selective decomposition according to the general equation



in which the Δ^5-dihydropyran-2-carboxylic acid compound or ester appears on the left-hand side of the equation and the alpha,beta-unsaturated carboxylic acid ester produced by the pyrolysis, along with unsaturated carbonylic compound produced as a by-product, appears on the right.

While it is known that, in the case of dihydro-1,4-pyran per se the heterocyclic ring can be broken by pyrolysis, it was unexpected to discover, and in our opinion could not have been foretold from the prior art that, the esters of Δ^5-dihydropyran-2-carboxylic acids which are employed in accordance with the process of the present invention could be selectively converted by controlled pyrolysis to the esters of alpha,-beta-olefinic open-chain carboxylic acids actually isolated as products of the present process. Whereas the ester linkage in esters of low molecular weight fatty acids with methanol, e. g., methyl acetate or even methyl benzoate, is relatively stable at elevated temperatures, even in some cases up to about red heat, esters of higher alcohols having a hydrogen atom attached to the beta carbon atom of the oxy radical of the alcohol component, are well-known to decompose under pyrolytic conditions to the free carboxylic acid component and an olefin derived from the alcohol component. Even if the ester with a higher alcohol contains no hydrogen atom

2

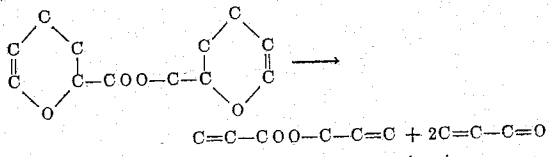
linked to a carbon atom in the beta position of the residue of the alcohol, the ester linkage is known to be unstable under conditions of pyrolysis, for example, as in the pyrolytic decomposition of benzyl benzoate which contains no beta hydrogen atom in the benzyl radical. Because the esters which are pyrolyzed in accordance with the present invention not only contain the heat-labile ester linkage, but, due to their complex structure, also present numerous possibilities for thermal isomerization or rearrangement, it could not, in our opinion, have been foretold that their selective pyrolysis to the products actually produced could be accomplished or that the products isolated would be formed in the desirably high yields actually observed.

The experiments which have been performed by the present inventors as a consequence of their invention have led to the conclusion that any monohydric alcohol ester of a Δ^5-dihydropyran-2-carboxylic acid can be pyrolyzed by the present process to produce an ester of an aliphatic or open-chain alpha,beta-olefinic carboxylic acid according to the generic equation described hereinbefore. By unmodified reference to "a Δ^5-dihydropyran-2-carboxylic acid" or to "the Δ^5-dihydropyran-2-carboxylic acids" in the present specification and claims, it is intended to include not only Δ^5-dihydropyran-2-carboxylic acid per se, the genotype or primary member of the class, but also its various substitution products, such as those obtained by replacing one or more of the hydrogen atoms linked to the carbon atoms of the ring or cycle by one or more hydrocarbon group or groups, preferably by one or more alkyl group or groups. From the standpoint of preparative convenience, low cost, adaptability to the present process, and favorable yields of desired products obtained therefrom, particularly preferred esters are the monohydric alcohol esters of Δ^5-dihydropyran-2-carboxylic acid and of the 2-alkyl- and 2,5-dialkyl-Δ^5-dihydropyran-2-carboxylic acids, such as of 2-methyl-Δ^5-dihydropyran-2-carboxylic acid, 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylic acid, 2,5-dineopentyl-Δ^5-dihydropyran-2-carboxylic acid, 2,5-dioctyl-Δ^5-dihydropyran-2-carboxylic acid, 2,5-dicyclohexyl-Δ^5-dihydropyran-2-carboxylic acid, and homologs and analogs thereof. Representative of the esters of the foregoing and like Δ^5-dihydropyran-2-carboxylic acids which can be pyrolyzed according to the process of the invention are the methyl, ethyl, propyl, butyl, actyl, lauryl, stearyl, allyl, methallyl, crotyl, alpha-neopentyl-

allyl, oleyl, oleostearyl, methoxyethyl, ethoxyethyl, phenyl, benzyl, cyclohexyl, cyclopentyl, and the like.

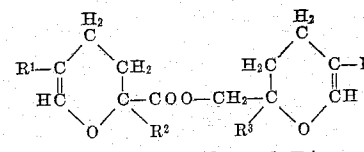
Depending upon the character of the oxy radical of the alcohol componet of the Δ^5-dihydropyran-2-carboxylic acid ester, the olefinic carboxylic acid ester obtained from the pyrolysis may or may not contain the same alcohol component. For example, the pyrolysis according to the invention of ethyl Δ^5-dihydropyran-2-carboxylate produces ethyl acrylate along with acrolein as a by-product. Isopropyl 2-methyl-Δ^5-dihydropyran-2-carboxylate is converted according to the invention to isopropyl methacrylate, with acrolein being formed as a by-product, and methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate is converted to methyl methacrylate, while methacrolein is produced as a by-product. As a still further example, the pyrolysis according to the invention of benzyl 6-methyl-Δ^5-dihydropyran - 2 - carboxylate produces benzyl acrylate with methyl vinyl ketone being formed as a by-product. On the other hand, if the oxy radical of the alcohol component is thermally unstable, it may undergo thermal reaction apart from the essential reaction accomplished in the process.

The process of the present invention is of particular value for the preparation of esters of alpha,beta-olefinic carboxylic acids with beta,-gamma-olefinic monohydric alcohols, such as allyl acrylate and methallyl methacrylate, by controlled pyrolysis of esters of Δ^5-dihydropyran-2-carboxylic acids with Δ^5-dihydropyran-2-methanols. It has been discovered in accordance with the present invention that the 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylates are converted by controlled pyrolysis with negligible (if any) cleavage of the ester linkage or other undesired side reactions, to valuable esters of open-chain unsaturated acids with open-chain unsaturated alcohols according to the general equation:



$$C{=}C{-}COO{-}C{-}C{=}C + 2C{=}C{-}C{=}O$$

in which the heterocyclic ester reactant appears on the left side of the equation and the unsaturated open-chain ester appears on the right. Preferred 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylates which are employed in accordance with this more limited aspect of the invention have structures that correspond to the general formula



where each of R^1, R^2, R^3, and R^4 represents a member of the class consisting of the hydrogen atom and the hydrocarbon radicals, preferably the alkyl radicals. R^1, R^2, R^3, and R^4 may be the same or they may be different. Preferably R^1 and R^4 are the same and R^2 and R^3 are the same, and most desirably R^1, R^2, R^3, and R^4 represent the same radical, that is, either the hydrogen atom or the same hydrocarbon radical, e. g., alkyl group.

Illustrative pyrolytic reactions which may be conducted according to the process of the invention employing esters within this preferred group are as follows: the pyrolysis of 2-(Δ^5-dihydropyranyl)-methyl Δ^5-dihydropyran-2-carboxylate to produce allyl acrylate; the pyrolysis of 2-(2,5-dimethyl - Δ^5 - dihydropyranyl) methyl 2,5 - dimethyl-Δ^5-dihydropyran-2-carboxylate to produce methallyl methacrylate; the pyrolysis of 2-(2-methyl-Δ^5-dihydropyranyl) methyl 2-methyl-Δ^5-dihydropyran - 2 - carboxylate to produce methallyl methacrylate; the pyrolysis of 2-(2,5-diethyl-Δ^5-dihydropyranyl) methyl 2,5 - diethyl-Δ^5-dihydropyran-2-carboxylate to produce beta-ethylallyl alpha-ethylacrylate; the pyrolysis of 2-(2,5 - dipropyl-Δ^5-dihydropyranyl) methyl 2,5-dipropyl-Δ^5-dihydropyran-2-carboxylate to produce beta-propylallyl alpha-propylacrylate; the pyrolysis of 2 - (2,5-diisopropyl-Δ^5-dihydropyranyl)-methyl 2,5-diisopropyl-Δ^5-dihydropyran-2-carboxylate to produce beta-isopropylallyl alpha-isopropylacrylate; the pyrolysis of 2-(2,5-dibutyl-Δ^5-dihydropyranyl) methyl 2,5 - dibutyl-Δ^5-dihydropyran-2-carboxylate to produce beta-butylallyl alpha-butylacrylate; the pyrolysis of 2-(2,5-diisobutyl-Δ^5-dihydropyranyl) methyl 2,5-diisobutyl-Δ^5-dihydropyran-2-carboxylate to produce beta-isobutylallyl alpha-isobutylacrylate; the pyrolysis of 2-(2,5-di-tertiary-butyl-Δ^5-dihydropyranyl) - methyl 2,5-di-tertiary-butyl-Δ^5-dihydropyran-2-carboxylate to produce beta-tertiary-butylallyl alpha-tertiary-butylacrylate; the pyrolysis of 2-(2,5-dipentyl-Δ^5-dihydropyranyl) methyl 2,5 - dipentyl-Δ^5-dihydropyran-2-carboxylate to produce beta-pentylallyl alpha-pentylacrylate; the pyrolysis of 2-(2,5-dihexyl-Δ^5-dihydropyranyl) methyl 2,5 - dihexyl-Δ^5-dihydropyran-2-carboxylate to produce beta-hexylallyl alpha-hexylacrylate; the pyrolysis of 2-(2,5-dioctyl - Δ^5 - dihydropyranyl) methyl 2,5-dioctyl-Δ^5-dihydropyran-2-carboxylate to produce beta-octylallyl alpha-octylacrylate; and the pyrolysis of 2-(2,5-didecyl-Δ^5-dihydropyranyl) methyl 2,5-didecyl-Δ^5-dihydropyran-2-carboxylate to produce beta-decylallyl alpha-decylacrylate.

The process is of particular interest for the preparation of esters of beta-alkyl allyl alcohols with their respective isologous alpha-alkyl acrylic acids, that is, such esters wherein the carbon skeleton is symmetrical about the oxy oxygen atom of the carbonyloxy group. While the process of the invention is applicable to the preparation of allyl acrylate, higher conversions to and yields of the alkyl-substituted esters ordinarily are obtained, wherein the ester products have the general formula

$$CH_2{=}C(R){-}CO{-}O{-}CH_2{-}C(R){=}CH_2$$

in which the R's represent like hydrocarbon groups, such as like alkyl groups. This was a surprising result of application of the process of the invention to the alkyl-substituted dihydropyran esters of the foregoing preferred class, since from theoretical considerations it would have been expected that those esters containing alkyl groups in the No. 2 or the Nos. 2 and 5 positions of the dihydropyran rings would be more stable than and have less tendency to undergo pyrolytic decompositon in the desired manner than the esters which are unsubstituted on the dihydropyranyl groups. The unsaturated aldehyde formed as a by-product can be separated from the unsaturated ester produced as the desired product and reconverted according to the method described herein, to a further amount of the 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydro-

pyran-2-carboxylate that was employed as the starting material in the pyrolysis. The process of the present invention has the unique advantage that, by employing such a cyclic mode of operation, the unsaturated aldehyde formed as a by-product eventually is substantially fully converted to the unsaturated ester desired as the product. Additional amounts of the open-chain unsaturated aldehyde may be supplied from an outside source to the cyclic operations and can be converted in an efficient and improved manner to the desired ester product. In essence, there is obtained by virtue of the cyclic operation, a new and improved process for converting in high yields and conversions alpha,beta-olefinic aldehydes to esters of alpha-beta-olefinic carboxylic acids with beta,gamma-olefinic alcohols.

In accordance with a preferred aspect of the invention the pyrolysis is conducted by subjecting vapors of the esters of the Δ^5-dihydropyran-2-carboxylic acids, or gaseous mixtures comprising vapors of the esters of the Δ^5-dihydropyran-2-carboxylic acids and an inert diluent gas, such as nitrogen, methane, hexane, carbon dioxide, carbon monoxide, steam, helium or the like, to the action of heat within a reaction zone maintained at a temperature sufficient to effect the desired pyrolytic reaction but below a temperature at which there would occur undesired side reactions, polymerization, carbonization, or the like. The pyrolysis preferably is effected at a temperature above about 250° C. and desirably within the range of from about 350° C. to about 750° C. The pyrolysis may be conducted at the atmospheric pressures or at pressures above or below atmospheric pressure. Pressures not substantially greater than atmospheric are preferred.

In general, any apparatus of a type suitable for carrying out pyrolytic processes of the present character may be employed. The esters which are pyrolyzed in accordance with the invention, as well as the unsaturated esters produced as products, are readily polymerized in liquid phase under the influence of heat. It has been found to be essential for optimum yields of and conversion to the desired products to minimize residence of the ester reactant in liquid state at the pyrolysis temperature. In order to accomplish this, the ester can be volatilized at a lower temperature into a stream of inert diluent gas and the gaseous mixture thereafter passed into and through the pyrolysis zone. According to another mode of executing the process of the invention, the liquid ester reactant can be passed in liquid phase to a zone wherein it is rapidly and substantially completely vaporized at or about the pyrolysis temperature and the resulting vapors retained in the reaction zone for any requisite additional time, and the products withdrawn from the zone substantially as rapidly as formed. The ester may be led onto a heated surface maintained at a temperature within the operable limits for the pyrolysis, thereby effecting substantially simultaneous volatilization and pyrolysis of the ester. A preferred procedure by means of which polymerization of the ester reactant may be minimized or substantially precluded, comprises introducing the liquid ester, which may be moderately preheated, in finely divided form, as by atomization or spraying, into a reaction zone heated to the pyrolysis temperature. By employing an efficient atomizer or spray, which may be of any suitable known type, minute droplets of the ester are rapidly dispersed into the heated

zone in heat exchange relation with the gaseous contents thereof, providing substantially instantaneous volatilization of the liquid reactant with resulting minimal undesired polymerization. The reaction zone may be defined by a heated enclosure or vessel provided with means for withdrawal of evolved vapors or the liquid ester may be atomized into a heated stream of an inert gas wherein it is vaporized and carried through a further space or reaction zone, such as provided by a heated elongated tube.

The pyrolysis of the esters of the Δ^5-dihydropyran-2-carboxylic acids may be conducted in the presence of inert solids, such as silicon carbide, pumice, or the like, disposed in the cracking or pyrolysis zone or in the presence of catalysts, such as activated alumina, silica gel, activated carbon, etc. Because better results ordinarily are obtained by conducting the pyrolysis in the absence of catalysts, the non-catalytic pyrolysis is preferred. The presence of inert solid contact materials is not excluded from such non-catalytic processes.

The products of the pyrolysis preferably are withdraw from the pyrolysis zone substantially as rapidly as formed and may be condensed and separated according to applicable known methods. Condensation of the gaseous reactor effluent may be accomplished with the aid of refrigeration, and/or by compression. In the pyrolysis of 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate, since acrolein distills at approximately 52° C. under 1 atmosphere pressure and allyl acrylate distills at about 122° C. under 1 atmosphere or at about 51° C. under 50 millimeters of mercury pressure, the ester product can readily be separated from acrolein formed as a by-product by fractional distillation of the condensed products, by fractional condensation of the gaseous product stream issuing from the reaction zone, or by like applicable methods. The unsaturated aldehyde formed as a by-product may be recovered as a separate fraction during the condensation of the reactor effluent or by subsequent treatment of the condensed products.

The esters of Δ^5-dihydropyran-2-carboxylic acids which are utilized in accordance with the present invention may be obtained or synthesized by any convenient available method. A preferred method comprises condensing an alpha,-beta-olefinic aldehyde, preferably an alpha-methylene aldehyde having the structure

$$CH_2=C(R)-CHO$$

in which R represents the hydrogen atom or a hydrocarbon group, such as an alkyl group, in liquid phase at a temperature desirably within the range of from about 100° C. to about 250° C., preferably from about 140° C. to about 200° C., in the presence of a phenolic antioxidant or polymerization inhibitor, such as hydroquinone. Suitable alpha-methylene aldehydes which may be employed include, among others, acrolein, methacrolein, alpha-ethylacrolein, the alpha-butylacroleins, the alpha-pentylacroleins, the alpha-hexylacroleins, alpha-phenylacrolein, alpha-cyclohexylacrolein, and the like, and their homologs and analogs. The Δ^5-dihydropyran-2-carboxaldehyde formed by the condensation of the alpha-methylene aldehyde may be converted to the corresponding Δ^5-dihydropyran-2-carboxylic acid by oxidation of the formyl group to carboxyl according to suitable applicable procedures, for example, by treatment with an oxygen-containing gas in the presence of an oxida-

tion catalyst, by treatment with predominantly chemical oxidizing agents, such as silver oxide, or like methods. For the oxidation of Δ^5-dihydropyran-2-carboxaldehyde to Δ^5-dihydropyran-2-carboxylic acid, a preferred oxidizing agent is silver oxide. Δ^5-Dihydropyran-2-carboxaldehydes bearing a substituent, such as an alkyl group, in the No. 2 position of the ring, which aldehydes are in general chemically more resistant than Δ^5-dihydropyran-2-carboxaldehyde, can be oxidized to the corresponding acids under somewhat more drastic conditions of reaction. For example, the substituted dihydropyran aldehyde conveniently may be converted to the corresponding dihydropyran carboxylic acid by treatment with a caustic alkali, such as an alkali metal hydroxide preferably in the form of a 20% to 50% aqueous solution, and separating the resulting dihydropyran carboxylic acid from the dihydropyran-2-methanol concurrently formed as a by-product of the reaction. Esters of the Δ^5-dihydropyran-2-carboxylic acids may be prepared from the free acids or suitable derivatives thereof, e. g., salts, by known applicable methods for the preparation of esters. In some cases the desired ester may be prepared conveniently by reaction between the appropriate hydrocarbon halide and a salt, such as the silver or sodium salt, of the dihydropyran carboxylic acid.

2-(Δ^5-dihydropyranyl)methyl Δ^5-dihydropyran-2-carboxylates which are employed in accordance with a preferred aspect of the present invention may be prepared conveniently by condensing Δ^5-dihydropyran-2-carboxaldehydes by treatment thereof in liquid phase with a lower alcoholate of a polyvalent metal of the second period of the periodic table of the elements, preferably an aluminum lower alkoxide, such as aluminum ethoxide, aluminum propoxide, aluminum isopropoxide, aluminum butoxide, aluminum pentoxide, or aluminum hexoxide. The condensation of the Δ^5-dihydropyran-2-carboxaldehyde to produce an ester of a Δ^5-dihydropyran-2-methanol with a Δ^5-dihydropyran-2-carboxylic acid may be effected simply by mixing therewith in liquid phase a small amount of the metal alcoholate under substantially anhydrous conditions and maintaining the mixture at room temperatures or somewhat above, say from 20° C. up to about 70° C., until the desired condensation has occurred. As little as 0.05% by weight of the alcoholate based on the weight of the Δ^5-dihydropyran-2-carboxaldehyde is effective, and amounts within the range of from about 0.1% to about 4% generally are entirely adequate. Inert solvents may be present during the condensation of the dihydropyran carboxaldehyde although the reaction proceeds to give high yields of the desired ester even in the absence of added solvents.

The process of the present invention provides a new and useful method for converting unsaturated aldehydes of the general formula

$$CH_2=C(R)-CHO$$

to unsaturated esters of the general formula

$$CH_2=C(R)-COO-CH_2-C(R)=CH_2$$

in which formulas R represents the hydrogen atom or an alkyl group and the atoms or radicals designated by R are the same. Thus considered, the process of the present invention offers several noteworthy advantages over methods heretofore known. The process of the present invention is characterized by improved efficacy, by better yields and by higher conversions of the unsaturated aldehyde to the desired unsaturated ester than have been attained according to the heretofore known methods. The alpha,-beta-unsaturated aldehyde is the only organic reactant employed, thereby simplifying not only the procurement of the necessary raw materials, but also the recovery of unreacted reactant from intermediate or final reaction mixtures. The only reagents other than the unsaturated aldehyde which need be supplied are the trace of polymerization inhibitor present during the condensation of the unsaturated aldehyde and the trace of aluminum or like alcoholate employed as catalyst for the conversion of the dihydropyran aldehyde to the 2-(Δ^5-dihydropyranyl)methyl Δ^5-dihydropyran-2-carboxylate. The process is conducted throughout in liquid phase except for the pyrolysis of the Δ^5-dihydropyran-2-carboxylic acid ester. As a further advantage, purification of the intermediates is not required although it is not precluded. Ordinarily the intermediate reaction mixtures may, at the most, be subjected to a partial distillation or topping operation to remove any lower boiling unreacted reactant present. By obviating the necessity for expensive and complex purification procedures for separation or purification of intermediates, the economy and efficacy of the process relative to prior art processes are substantially enhanced. At no point during the cyclic operations is it necessary to employ a solvent or other dispersing medium. This feature of the invention further simplifies the necessary operating procedures and contributes to the practical value of the process for operation on a large scale. Other advantages of the process of the invention will be apparent from the more general disclosures herein.

The following examples will serve to illustrate certain specific embodiments of the process of the invention. It will be understood that the examples are intended to be illustrative of the invention and not limitations thereon, as it is more broadly disclosed herein and defined in the hereto appended claims. In the examples, the parts are by weight.

Example I

Preparation of 2-(2,5-dimethyl-Δ^5-dihydropyranyl)methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate.—For the preparation of 2,5-dimethyl-Δ^5-dihydropyran-2-carboxaldehyde from methacrolein there was employed an apparatus which comprised a vertically-positioned heated reaction tube constructed of stainless steel and having an internal diameter of ⅝ inch and a length of 40 inches. The reaction tube was surrounded by electrical heating elements and had a ¼ inch diameter thermocouple well extending coaxially throughout its length. The free space within the tube was approximately 185 cc. A reservoir for liquid reactor feed was connected through a preheater to the lower end of the tube. A source of nitrogen under high pressure was connected to the reservoir for forcing the feed through the reaction tube under pressure. The upper end of the reaction tube was connected through an adjustable pressure-relief valve by means of which the pressure on the reactor effluent was let down to approximately atmospheric, to a water-cooled condenser in which gaseous components of the effluent were condensed and collected.

A stream of liquid methacrolein containing 1% by weight of hydroquinone was passed through the reaction tube at a temperature of 210° C. and a rate of flow of 1.28 reciprocal hours (volumes liquid per volume reaction space per hour) under a pressure of 600 pounds per square inch. After a brief initial time during which a steady state was established, the mixture leaving the tube was collected and fractionally distilled. 2,5-dimethyl-Δ^5-dihydropyran-2-carboxaldehyde was recovered from the mixture as a fraction distilling at about 100° C. to 102° C. under a pressure of 90 millimeters of mercury in an amount corresponding to a yield based upon methacrolein consumed of 95% and in a conversion of methacrolein to product of 75%.

For the preparation of 2-(2,5-dimethyl-Δ^5-dihydropyranyl) methyl - Δ^5 - dihydropyran - 2 - carboxylate, there were added to 50 parts of 2,5-dimethyl - Δ^5 - dihydropyran - 2 - carboxaldehyde with stirring three parts of aluminum isopropoxide. The mixture was allowed to stand at room temperature for about 16 hours. By distillation of the resulting mixture there was separated a fraction distilling at 110° C. to 116° C. under a pressure of 0.5 millimeter of mercury, corresponding to a 75% conversion of the 2,5-dimethyl-Δ^5-dihydropyran-2-carboxaldehyde to 2-(2,5-dimethyl-Δ^5-dihydropyranyl) methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate.

Pyrolysis of 2-(2,5-dimethyl-Δ^5-dihydropyranyl) methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate.—Two hundred eight parts of the 2-(2,5-dimethyl-Δ^5-dihydropyranyl) methyl 2,5-dimethyl-Δ^5-dihydropyran -2-carboxylate were passed during 190 minutes at a velocity of 0.70 volume of liquid feed per volume of reaction space per hour, downwardly through a stainless steel tube packed with silicon carbide chips and electrically heated to 475° C. The gaseous effluent was withdrawn from the pyrolysis tube as formed, condensed in a water-cooled condenser and a small amount of hydroquinone was added to the condensate to inhibit polymerization. Distillation of 200 parts of the condensate, containing hydroquinone, resulted in the recovery of the following fractions:

A. 92 parts distilling at 63.6° C. to 69.6° C. under atmospheric pressure (methacrolein).
B. 91 parts distilling at 60.6° C. to 82.4° C. under 50 millimeters' mercury (methallyl methacrylate).

The methacrolein fraction can be recycled to the first step of this example, along with an additional amount of methacrolein if desired, and thereby converted to a further quantity of methallyl methacrylate. The methallyl methacrylate fraction corresponds to an 87.5% yield of and conversion to product based upon the amount of 2-(2,5-dimethyl-Δ^5- dihydropyranyl) methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate consumed and applied, respectively.

Example II

Preparation of 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate. — Δ^5 - dihydropyran-2-carboxaldehyde was prepared from acrolein in the apparatus employed for the condensation of methacrolein in Example I. A stream of liquid acrolein containing 1% by weight of hydroquinone was passed through the reaction tube at a temperature of 190° C., a flow rate of 2.1 reciprocal hours, and under a pressure of 480 to 580 pounds per square inch. After a steady state was established the reactor effluent was collected and fractionally distilled. The Δ^5-dihydropyran-2-carboxaldehyde was recovered in a yield of 92% based upon the acrolein consumed as a fraction distilling at about 88° C. under 100 millimeters mercury pressure.

To 500 parts of Δ^5-dihydropyran-2-carboxaldehyde thus prepared there were added 2.5 parts by weight of aluminum isopropoxide as a solution in carbon tetrachloride containing 0.5 gram aluminum isopropoxide per cubic centimeter of solution. The mixture was stirred to distribute the aluminum isopropoxide throughout and then allowed to stand. Gentle evolution of heat warmed the mixture to 30° C. to 40° C. and the temperature thereafter was maintained in this range by cooling as required. After a reaction time of 4 hours, the mixture was fractionally distilled with separation of 2-(Δ^5-dihydropyranyl) - methyl Δ^5-dihydropyran-2-carboxylate in a yield of 75% of theory as the fraction distilling between 115° C. and 125° C. under a pressure of 0.5 millimeter of mercury.

Pyrolysis of 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate.—For the pyrolysis in this experiment there was employed a reactor consisting of an electrically heated vertically positioned glass ("Pyrex") tube having an internal diameter of 21 millimeters and a length of 1000 millimeters. In the top of the tube there was inserted a short cylinder of nichrome screen surmounted by a glass dome having an outside diameter of 20 millimeters, on which the feed was dropped to promote even distribution over and on the reactor walls. One hundred thirteen parts of 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate were passed downwardly through the glass tube by dropping onto the top of the glass dome at a rate of 0.155 liquid volumes of ester per volume of reaction space per hour, and withdrawing product from the lower end of the tube. The pyrolysis temperature was 470° C. to 475° C. The condensed product, inhibited by addition of hydroquinone, was fractionally distilled through a short column with collection of the following fractions:

a. 40 parts distilling at 49° C. to 51° C. under 1 atmospheric pressure (acrolein).
b. 35 parts distilling at 51.6° C. to 60° C. under 50 millimeters' mercury pressure (allyl acrylate).
c. 10 parts distilling at 42.5° C. under 5 millimeters' mercury pressure to 67° C. under 2 millimeters' mercury pressure (intermediate cut).
d. Bottoms, 3 parts.

By further pyrolysis of fraction *c*, the intermediate cut, there was obtained an additional quantity of allyl acrylate. Instead, the intermediate cut can be added to a further quantity of the 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate and pyrolyzed therewith rather than in a separate operation. Good conversions of the intermediate cut to allyl acrylate can be obtained.

Example III

From a dropping funnel in the top of a Claisen flask, 82 grams of 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate were dropped in the course of 125 minutes onto the bottom of the flask which was heated by means of a Wood's metal bath at 465° C. The product, which distilled continuously at 119° C. to 131° C., weighed 76 grams. There remained 7 grams of residue in the reactor flask. The distillate, inhibited by

hydroquinone, was distilled through a packed column to obtain the following fractions:

a. 29 grams (acrolein).
b. 20.5 grams (allyl acrylate).
c. 8 grams (intermediate product).
d. Residue, 6.5 grams.

Example IV

One hundred thirty-one parts by weight of 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate were pyrolyzed by downward passage through a vertically positioned unpacked electrically heated glass tube at a temperature of 450° C. and a feed rate of 1.09 grams per minute. By withdrawing and condensing the products from the lower end of the tube and fractionally distilling the condensate inhibited by the addition of hydroquinone, allyl acrylate was obtained in a conversion of 43% based upon the amount of 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate applied.

Example V

When the foregoing experiment was repeated employing an additional 199 parts of 2-(Δ^5-dihydropyranyl) methyl Δ^5 - dihydropyran - 2 - carboxylate, a temperature of 470° C. to 475° C. and a feed rate of 1.20 grams per minute, the conversion of the ester to allyl acrylate was increased to 55.3% of theory.

Example VI

Ethyl Δ^5-dihydropyran-2-carboxylate, which had been prepared by oxidation of Δ^5-dihydropyran-2-carboxaldehyde to Δ^5-dihydropyran-2-carboxylic acid with silver oxide and reaction of the silver salt of the acid with ethyl iodide, was pyrolyzed at about 500° C. by dropping at a feed rate of 0.58 gram per minute into a heated Claisen flask immersed in a bath of molten Wood's metal and condensing the products which distilled substantially as rapidly as formed. Ethyl acrylate was obtained by fractional distillation of the condensed products in a conversion of 77.5% of theory.

The disclosures of this application include subject matter which is disclosed and/or claimed in the following applications to which reference is hereby made: Serial No. 713,455, filed December 2, 1946, by R. R. Whetstone, now Patent No. 2,479,283; Serial No. 706,102, filed October 28, 1946, by R. R. Whetstone, S. A. Ballard and C. J. Ott, now Patent No. 2,514,172; Serial No. 735,029, filed March 15, 1947, by R. R. Whetstone, now Patent No. 2,479,284; Serial No. 51,483, filed September 27, 1948, by C. W. Smith, now Patent No. 2,537,921.

The claimed invention is:

1. A process for the preparation of methallyl methacrylate, which comprises pyrolyzing 2-(2,5-dimethyl - Δ^5 - dihydropyranyl) methyl 2,5 - dimethyl - Δ^5 - dihydropyran - 2 - carboxylate non-catalytically at a temperature within the range of from about 350° C. to about 750° C. and recovering methallyl methacrylate from the products of the pyrolysis.

2. A process which comprises pyrolyzing 2-(2,5-dimethyl - Δ^5 - dihydropyranyl) methyl 2,5 - dimethyl - Δ^5 - dihydropyran - 2 - carboxylate at a temperature within the range of from about 250° C. to about 750° C. to produce methallyl methacrylate.

3. A process for the preparation of allyl acrylate, which comprises pyrolyzing 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate non-catalytically at a temperature within the range of from about 350° C. to about 750° C. and recovering allyl acrylate from the products of the pyrolysis.

4. A process which comprises pyrolyzing 2-(Δ^5-dihydropyranyl) methyl Δ^5-dihydropyran-2-carboxylate non-catalytically at a temperature within the range of from 250° C. to about 750° C. to produce allyl acrylate.

5. A process for the preparation of methallyl methacrylate, which comprises pyrolyzing 2-(2,5-dimethyl-Δ^5-dihydropyranyl) methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate in vapor phase in the presence of an inert diluent gas at a temperature within the range of from about 350° C. to about 750° C.

6. A process for the preparation of allyl acrylate, which comprises pyrolyzing 2-(Δ^5-dihydropyranyl) methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate in vapor phase in the presence of an inert diluent gas at a temperature within the range of about 350° C. to about 750° C.

7. A process for the preparation of methallyl methacrylate, which comprises atomizing 2-(2,5-dimethyl-Δ^5-dihydropyranyl) methyl 2,5-dimethyl-Δ^5-dihydropyran-2-carboxylate into a heated stream of an inert gas and conveying the gaseous stream through a pyrolysis zone maintained within the range of from about 350° C. to about 750° C.

8. A process for the controlled pyrolysis of an ester of a Δ^5-dihydropyran-2-carboxylic acid with a Δ^5-dihydropyran-2-methanol to selectively produce a valuable polymerizable ester of an open-chain alpha,beta-olefinic carboxylic acid with an open-chain beta,gamma-olefinic alcohol, which comprises rapidly heating said heterocyclic ester while in liquid state toward a temperature within the range of from about 350° C. to about 750° C., simultaneously with said heating flashing the ester from liquid phase to gaseous phase, subjecting said gaseous phase to controlled pyrolysis within the range of from about 350° C. to about 750° C. and recovering a polymerizable ester of an open-chain alpha,beta-olefinic carboxylic acid with an open-chain beta,gamma-olefinic alcohol from the products of the pyrolysis.

9. A process which comprises pyrolysis of an ester of a Δ^5-dihydropyran-2-carboxylic acid with a Δ^5-dihydropyran-2-methanol at a temperature within the range of from about 350° C. to about 750° C. to produce an ester of an open-chain alpha,beta-olefinic carboxylic acid with an open-chain beta,gamma-olefinic alcohol.

10. A process for the preparation of ethyl acrylate, which comprises pyrolyzing ethyl Δ^5-dihydropyran-2-carboxylate at a temperature within the range of from about 350° C. to about 750° C.

11. A process which comprises non-catalytic pyrolysis of an alkyl Δ^5-dihydropyran-2-carboxylate at a temperature within the range of from about 250° C. to about 750° C. to produce an alkyl acrylate.

12. A process which comprises pyrolysis of an ester of a Δ^5-dihydropyran-2-carboxylic acid at a temperature within the range of from about 250° C. to about 750° C. to produce an ester of an open-chain alpha,beta-olefinic carboxylic acid.

RICHARD R. WHETSTONE.
WILLIAM J. RAAB.
SEAVER A. BALLARD.

(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,250,520	Bludworth	July 29, 1941
2,479,284	Whetstone	Aug. 16, 1949
2,516,627	Hearne et al.	July 25, 1950

OTHER REFERENCES

Hurd: The Pyrolysis of Carbon Compounds, 1929, page 364.