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PROCESS OF PREPARING ACETALS OF ACETYLENIC ALDEHYDES

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This invention relates to a method for the preparation of acetals of aliphatic acetylenic aldehydes and it is of particular value for the preparation of acetals of propargyl aldehyde, the lowest member of the homologous series. More particularly, the invention relates to a process for the dehydrohalogenation of acetals of aliphatic alpha-halo olefinic aldehydes to produce the corresponding acetylenic acetal, specifically, the dehydrochlorination of acetals of alpha-chloroacrolein to produce acetals of propargyl aldehyde.

An object of the present invention is an efficient and commercially practicable method for the preparation of acetals of aliphatic acetylenic aldehydes. A more limited object of the invention is a process for the preparation of acetals of propargyl aldehyde, the lowest and most valuable member of the class of aliphatic acetylenic aldehydes. Another object of the invention is a process for the conversion by dehydrochlorination of acetals of alpha-chloroacrolein to the corresponding acetals of propargyl aldehyde. A related object is a process for such conversion which is adapted to efficient and economic operation and which results in high yields of the acetylenic acetal. An important object of the invention is a process which results in minimal formation of tars, resins or polymers, or other products other than the desired acetylenic acetal. Other objects of the invention will become apparent hereinafter.

According to the process of the invention, broadly stated, acetals of acetylenic aliphatic aldehydes are prepared by treating the corresponding acetals of alpha-halo olefinic aliphatic aldehydes with an aqueous solution of an alkali under a superatmospheric pressure and at a temperature above the boiling point of the solution under atmospheric pressure, and recovering the desired acetylenic acetal from the reaction mixture. According to preferred practice, the process of the invention is executed with continuous wthdrawal in the vapor phase under the superatmospheric pressure, of the acetylenic aldehyde acetal formed by the dehydrohalogenation, at a rate that is substantially equal to the rate of its formation in the process. The process of the invention is of value for the reason, among others, that it makes possible the preparation in a greatly improved manner acetals of propargyl aldehyde from acrolein. Prior to the present invention there was no practicable method known for the conversion of acetals of alpha-halo olefinic aliphatic aldehydes, e. g., acetals of alpha-chloroacrolein, to the corresponding acetals of the acetylenic aldehyde. Accordingly, acetals of propargyl aldehyde, and of certain of

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its lower straight chain homologs, have been prepared heretofore by brominating, for example, acrolein to obtain acrolein dibromide, preparing the acetal of the dibromoaldehyde, as by reaction thereof with an ester of orthoformic acid, and then removing two molecules of hydrobromic acid from the dibromoacetal. However, the direct preparation of the acetals of the dibromo aldehydes has proved quite troublesome and capable of accomplishment only with relatively low yields of the desired product or at prohibitive cost. Furthermore, the dehydrobromination of the dibromo aldehyde acetals entails undesirable features and the yields of the acetylenic aldehyde acetals are undesirably low. This is due to the fact that in the prior art processes the dehydrobromination of the dibromo aldehyde acetals forms complex mixtures of products from which the desired acetylenic aldehyde acetal can be separated only with great difficulty. Because of the excessive formation of products of side reactions, the yield of the desired acetylenic aldehyde acetal, based upon the essentially complete consumption of the dibromo aldehyde acetal, is excessively low.

Acetals of the alpha-halo acroleins may be prepared efficiently and conveniently by halogenating acrolein according to known processes to obtain the dihalopropionaldehyde which may be dehydrohalogenated to the alpha-halo acrolein, as by adding it to boiling water and distilling an azeotropic mixture of the alpha-halo acrolein and water. The acetals of the monohalo olefinic aldehydes may be prepared conveniently and in excellent yields by reaction between the aldehyde and a suitable alcohol at about room temperature, preferably catalyzed by a trace of acidic catalyst. By providing for the first time a practicable method for the removal of hydrogen halide from these monohalo olefinic acetals, the process of the present invention makes it possible to avoid the difficulties that have been associated with the prior art processes. The process of the present invention, therefore, makes possible the conversion of acrolein to acetals of propargyl aldehyde in a greatly improved and a highly efficient manner with high over-all yields of the desired product.

The process of the present invention is executed by treating an acetal of a suitable alpha-halo-alpha,beta-olefinic aliphatic aldehyde with an aqueous solution of an alkali under a superatmospheric pressure at a dehydrohalogenation temperature above the normal boiling point of the alkali solution, and recovering the corresponding acetylenic aldehyde acetal from the mixture. The process of the invention is distinctly different from the method proposed by

Claisen for the preparation of acetals of propargyl aldehyde. According to the method of Claisen an acetal of dibromopropionaldehyde is treated with an alcoholic solution of potassium hydroxide to remove two molecules of hydrobromic acid from the acetal. The process proposed by Claisen suffers from the disadvantage that, although the acrolein dibromide acetal is essentially completely consumed, no less than about 40 per cent of it is converted to products other than the desired propargyl aldehyde acetal. In other words, the process of Claisen results in the non-selective conversion of the dibromo aldehyde acetal to a mixture of products which contains an undesirably low proportion of the desired acetylenic acetal. It further has been found that the treatment of acetals of the aliphatic monohalo alpha,beta-olefinic aldehydes, for example, the diethyl acetal of alpha-chloroacrolein, with an alcoholic solution of a caustic alkali at a temperature and pressure within the range of temperatures and pressures that are employed in the execution of the process of the present invention results in the essentially complete conversion of the acetal to products which are distinctly different from those desired in accordance with the present invention, and with no detected formation of the desired acetylenic acetal. The dehydrohalogenation of the monohalo olefinic acetals by treatment according to the process of the present invention with aqueous solutions of alkalies, therefore, offers substantial and unexpected advantages over the dehydrohalogenation of the dihalo saturated aldehyde acetals by treatment with alcoholic solutions of potassium hydroxide. The advantages are due in part to the greatly improved yields of the acetylenic aldehyde acetal that may be obtained. In other words, the selectivity of the conversion has been greatly improved relative to the prior art processes for the preparation of such acetylenic aldehyde acetals. A further advantage of the process of the present invention is the greater ease and economy with which the dehydrohalogenation may be executed, particularly with respect to the recovery and purification of the desired acetylenic acetal. In the process of the invention, it is not necessary to resort to elaborate procedures necessary for separation of the acetal from an organic solvent. Furthermore, the use of aqueous solutions of alkalies under the conditions provided by the invention unexpectedly has been found to have the advantage of avoiding the excessive formation of undesired products of side-reactions which appear to be favored by the presence of an alcohol.

The alkalies which may be employed in the process of the invention may preferably be alkali metal alkalies, such as the carbonates of the alkali metals or the hydroxides of ammonium and of the alkali metals. We preferably employ the alkali-metal hydroxides. It has been suggested by Viguier to employ potassium hydroxide in the solid form to effect dehydrohalogenation of the diethyl acetal of dibromobutyraldehyde, but the observed results were not satisfactory because of the complex mixture of products that always was formed and the very poor yields of the desired acetylenic acetal. Not even the use of an alcoholic solution of potassium hydroxide was found to overcome the difficulties which attended such application of solid caustic potash. This was due to the low and variable yields that were obtained and because of the excessive formation of by-products whose removal from the desired acetylenic product was found to be extremely difficult and time-consuming. Unexpectedly, the dehydrohalogenation of monohalo olefinic acetals by treatment thereof with aqueous solutions of alkalies has been found to overcome these difficulties by providing high ultimate yields of the desired product, and by resulting in the formation of greatly reduced amounts of by-products, which by-products in any event easily may be separated from the desired acetylenic acetal. We prefer to employ aqueous solutions of sodium hydroxide in the process of the present invention. Aqueous solutions of other alkalies may be employed, however. Instead of an aqueous solution of sodium hydroxide, there thus may be employed aqueous solutions of other alkali hydroxides, such as of potassium hydroxide, lithium hydroxide, and even of rubidium and caesium and ammonium hydroxides. Aqueous solutions of hydroxides of the alkaline earth metals also may be employed in the process of the invention, e. g., barium hydroxide, calcium hydroxide, and strontium hydroxide. Less desirably, aqueous solutions of alkali metal carbonates, e. g., sodium carbonate, may be employed. As a general rule, the most favorable results may be obtained by employing an aqueous solution of a caustic alkali, i. e., a hydroxide of an alkali metal. In the execution of the process of the invention, the aqueous solution of the alkali, regardless of the particular alkali that is employed, initially contains from about 2% to about 30% by weight of the alkali, and preferably from about 5% to about 30% by weight. The process of the invention may be executed in either a batchwise or continuous manner. In a batchwise application of the process, the aqueous alkali solution of the desired concentration simply may be made up and used without further or subsequent treatment. In application of the process to continuous operations, additional alkali in the form of either a solid or a more concentrated aqueous solution may be introduced into the reaction system to replenish the alkali that is consumed in the process, or the solution of the alkali may be withdrawn continuously or intermittently from the reaction zone and treated as necessary to restore its content of alkali to the original. The process of the invention has the advantage that the metal halide formed by reaction of the dissolved alkali with the hydrogen halide liberated from the alpha-halo olefinic acetal may remain in solution throughout the dehydrohalogenation step of the process. The presence of the metal halide in dissolved state greatly facilitates recovery of the desired product and, furthermore, obviates the use of the expensive and complex equipment that otherwise would be required to handle reaction mixtures containing large amounts of suspended or precipitated solids, as when an organic solvent reaction medium is employed. The metal halides may be removed from the reaction mixture by withdrawing all or a portion of the aqueous solution continuously or intermittently during the process and either replacing the withdrawn solution with a freshly made-up portion, or treating the withdrawn portion in any suitable known manner to separate the metal halide from the alkali.

The amount of the alkali solution that is employed in the process is not highly critical, bearing in mind, however, that the alkali is neutralized by the hydrogen halide liberated during the

reaction and that at least the stoichiometric equivalent of the alkali, therefore, should be present. It is preferred to employ a moderate excess of the alkali solution, e. g., an amount containing the alkali in at least about a 10% excess over the stoichiometric equivalent of the liberated hydrogen halide. We prefer to employ upwards from about 1.1 acid-equivalents of the alkali per mole of the olefinic aldehyde acetal. Much larger amounts may be used since the presence of a large excess of the alkali solution is not detrimental other than as it may, through its sheer bulk, unduly overload the reaction system. A convenient, but not a critical, maximum amount is about 10 moles of the alkali per mole of the olefinic aldehyde acetal.

The process of the invention is executed with the reaction mixture under a superatmospheric pressure and at a temperature above the normal boiling point of the aqueous alkali solution that is employed. A preferred range of pressures is from 40 pounds per square inch (gauge) to about 200 pounds per square inch (gauge). The upper limit of the pressure is not highly critical; for example, in batchwise operations considerably higher pressures may be employed. However, no particular advantage ordinarily is derived from the use of pressures substantially greater than about 200 pounds per square inch (gauge), and from the operating standpoint this value provides a convenient maximum. At pressures below 40 pounds per square inch (gauge) the conversion of the alpha-halo olefinic aldehyde acetal is substantially below the conversions that are obtained when operating under the higher pressures in accordance with the invention. Most efficient operations, therefore, are obtained by operating at pressures above 40 pounds per square inch (gauge). The minimum pressure that is employed is preferably not below about 10 pounds per square inch (gauge), since at pressures substantially below this pressure the conversion of the alpha-halo olefinic aldehyde acetal to the desired acetylenic aldehyde acetal is reduced below the level of practicable operations. The temperature that is employed must be sufficiently elevated to cause the desired dehydrohalogenation to occur, but not so high that thermal decomposition of either the olefinic or the acetylenic aldehyde acetal occurs. We have found that for practicable conversions of the alpha-halo olefinic acetal to the acetylenic acetal temperatures of at least about 110° C. desirably are employed and the temperature that is employed preferably should be at least about 130° C. The maximum temperature that is used is limited, in the broad case, to the temperature at which the total vapor pressure of the reaction mixture is equal to the pressure that is employed. Preferably, however, the temperature that is employed is not over about 190° C., although somewhat higher temperatures, say up to about 220° C., may at times be used. We have found that optimum results in conversion to and yield of the desired acetylenic acetal may be obtained by operating within the temperature range of from about 130° C. to about 170° C. The pressure conveniently may be the autogenous pressure of the reaction mixture at the temperature that is employed; however, in certain cases it may be desirable to operate at pressures somewhat above the autogenous pressure of the reaction mixture. In such cases, pressure may be applied to the reaction mixture by introduction of a suitable inert gas into the reaction zone. Suitable inert gases include, for example, nitrogen, helium, methane, ethane, etc.

The dehydrohalogenation is effected by contacting the alpha-halo olefinic aldehyde acetal with the aqueous alkali solution under the aforesaid conditions of elevated temperature and superatmospheric pressure. As indicated previously, the process may be executed in either a batchwise or a continuous manner. In a batchwise execution of the process, the aqueous alkali solution and the halogen-substituted acetal are introduced into a suitable pressure-resistant reaction vessel and heated for a sufficient time at the elevated temperature and pressure. The reaction mixture desirably is agitated vigorously during the heating to insure intimate contacts between the aqueous solution and the halogen-substituted acetal. Reaction times of from 1 to 6 hours are generally adequate. Unduly prolonged reaction times desirably are avoided because of the possibility that excessive side reactions would be favored. Reaction times not over about 3 hours are preferred. In a continuous manner of executing the process of the invention, a mixture in the desired proportions of the alpha-halo olefinic aldehyde acetal and the aqueous alkali solution may be passed through one or a plurality of zones maintained at a suitable temperature and pressure to effect the dehydrohalogenation. According to the preferred practice, the acetylenic acetal is separated in the vapor phase from the reaction mixture at a rate substantially equal to its rate of formation in the dehydrohalogenation reaction. The separation may be accomplished by adjusting the temperature and pressure to conditions such that the acetylenic acetal is volatilized from the liquid mixture of the aqueous alkali solution and the halogen-substituted olefinic aldehyde acetal, and continuously withdrawing the vapors of the acetylenic acetal from the reaction zone during the dehydrohalogenation treatment. In continuous operations, the separation of the vapors of the acetylenic acetal may be effected in one separating means, or a plurality of separating means may be employed, with partial separation in each. The vapors thus withdrawn may be condensed to recover the desired product, and any unreacted halogen-substituted acetal and/or water that may pass over therewith may be returned to the reaction zone. In other cases the dehydrohalogenation may be allowed to go to substantial completion prior to separation of the acetylenic acetal from the reaction mixture. The entire reaction mixture thus may be treated at the conclusion of the dehydrohalogenation treatment according to any suitable method to recover the desired acetylenic acetal. For example, the mixture may be cooled and allowed to stratify into two phases—one an aqueous phase and the other an organic phase containing the acetylenic metal. The two phases may be separated as by decantation, and the organic phase treated, as by fractional distillation, to recover the desired product. Any unreacted alpha-halo olefinic acetal and/or the aqueous alkali solution in whole or in part may be recirculated through the process, additional alkali being added to the aqueous solution as required.

The following examples will illustrate the invention that is defined in the appended claims. In the examples, the parts are by weight.

Example I

This example illustrates a preferred manner of executing the process of the invention and illustrates the manner in which the advantages of the

invention are realized in the preparation of an acetal of propargyl aldehyde from acrolein.

In this experiment, acrolein was chlorinated by passing a liquid stream countercurrent to a stream of gaseous chlorine flowing upwardy through a glass-helix packed column maintained at a temperature of about 25° C. The flow rates of the streams of acrolein and of chlorine were so adjusted that there was present an excess of chlorine about 10% over the amount theoretically required. The acrolein was introduced into the column at a rate of about 4 mols per hour.

The alpha,beta-dichloropropionaldehyde thus formed was led directly from the lower end of the column into boiling water, and the azeotropic mixture of water and alpha-chloroacrolein which distilled was condensed and then redistilled under a pressure of 30 millimeters of mercury, the fraction distilling between 31° and 32° C. being collected as the product.

The dimethyl acetal of the alpha-chloroacrolein was prepared by reaction between the alpha-chloroacrolein and methanol present in a 1:5 molar ratio. The reaction was catalyzed by adding a small amount of anhydrous HCl to the mixture. After 3 hours at 25° C., the acid was neutralized and the mixture distilled. The dimethyl acetal of alpha-chloroacrolein was recovered as the fraction distilling between 38° and 39° C. under a pressure of 20 millimeters of mercury. The yield of the acetal, based upon the alpha-chloroacrolein employed, was 82% of theory.

For the dehydrochlorination of the dimethyl acetal of alpha-chloroacrolein, there was employed a pressure-resistant reaction vessel adapted to be closed from the atmosphere, equipped with an efficient mechanical stirrer and means for heating the contents to a desired temperature. A steel dephlegmator was directly attached to the vessel, arranged for condensation at the reaction pressure of volatiles leaving the reaction mixture. The dephlegmator was surrounded by a jacket through which steam at atmospheric pressure was circulated for cooling, and was provided with a suitable trap and outlet valve for removal from the system of a desired fraction of the condensate.

One hundred parts of the alpha-chloroacrolein dimethyl acetal and 330 parts of a 15% by weight solution of sodium hydroxide in water were mixed in the reaction vessel. The vessel was closed from the atmosphere and the mixture was heated, with agitation, to a temperature of 146° C. under a pressure of 77 pounds per square inch (gauge). Product was taken overhead continuously as formed, by condensation in the dephlegmator, and withdrawn from the system. The condensate was found to be composed of a mixture of essentially pure propargyl aldehyde dimethyl acetal with water. The heating was discontinued after 70 minutes operation. The collected product was redistilled to recover the propargyl aldehyde dimethyl acetal. Under the conditions that were employed, the acetylenic acetal was obtained in a yield of 71% based upon the alpha-chloroacrolein dimethyl acetal consumed in the process, indicating the highly selective conversion of the halogen-substituted acetal to the acetylenic acetal that is obtained according to the process of the invention. In this experiment, the conversion of the alpha-chloroacrolein dimethyl acetal to the proargyl aldehyde acetal was about 35% of the amount employed. It is evident, because of the high yield that was obtained, that the conversion could have been increased substantially by prolonging the reaction time or by recycling unreacted alpha-chloroacrolein dimethyl acetal through the process.

Example II

For this experiment, the diethyl acetal of alpha-chloroacrolein was prepared by reacting alpha-chloroacrolein with ethanol in a manner similar to the method used in the preceding example. The halogen-substituted acetal was mixed in an autoclave with 2.24 times its weight of a 14% by weight solution of sodium hydroxide in water, and the mixture was heated for one hour, with agitation, to 160° to 165° C. under the autogenous pressure of the mixture. At the end of this time, the autoclave was cooled, and the mixture withdrawn and allowed to separate into two phases. The organic phase was separated from the aqueous phase and fractionally distilled. The diethyl acetal of propargyl aldehyde was thereby recovered in a yield of about 70% based upon the amount of the alpha-chloroacrolein diethyl acetal consumed. In this particular experiment, the conversion of the alpha-chloroacrolein diethyl acetal to propargyl aldehyde acetal was about 32%. When the experiment was repeated employing the same conditions except for a reaction time of two hours, the conversion to the propargyl aldehyde acetal was increased to 59% without significant change in the yield that was obtained, that is, without significant change in the selectivity of the process.

Example III

Although in the foregoing examples 14 to 15% solutions of the caustic alkali were employed, alkali solutions of substantially greater concentration may be used, as demonstrated by this experiment. In this experiment, 68 parts of the dimethyl acetal of alpha-chloroacrolein was mixed with 190 parts of a 23% by weight solution of sodium hydroxide in water, and the mixture was heated for 2 hours at 140° C. under the autogenous pressure of the mixture. The resultant mixture was withdrawn from the reaction vessel, the organic phase was separated as in the preceding example, and distilled. The dimethyl acetal of propargyl aldehyde was recovered in a yield of 70.5% based upon the alpha-chloroacrolein acetal consumed and in a conversion comparable to the conversions previously obtained.

Example IV

Instead of the sodium hydroxide employed in the preceding examples, potassium hydroxide may be used as the caustic alkali with similar results. For example, the dimethyl acetal of alpha-chloroacrolein may be mixed in an autoclave with 1.1 molar equivalents of potassium hydroxide in the form of a 15% by weight solution in water, and the mixture heated under the autogenous pressure for 2 hours at 150° C. The resultant mixture, when worked up as in the foregoing examples, contains the propargyl aldehyde acetal in yields corresponding to the yields observed in the previous experiments.

The process of the invention is of particular value for the preparation of acetals of propargyl aldehyde by the dehydrochlorination of acetals of alpha-chloroacrolein. This is due to the value of the products, i. e., the acetals of propargyl aldehyde, but also because of the characteristics of the acetals of alpha-chloroacrolein which render such acetals especially unamenable to efficient dehydrochlorination according to prior art

processes. To the best of our knowledge, there has not been proposed heretofore a practical method for the dehydrohalogenation of acetals of alpha-chloroacrolein. Although the invention, therefore, has been described and illustrated with particular reference to the conversion of acetals of alpha-chloroacrolein to acetals of propargyl aldehyde, acetals of homologous aliphatic alpha,-beta-acetylenic aldehydes may be prepared by the process from corresponding acetals of alpha-halo-alpha,beta-olefinic aldehydes, e. g., acetals of tetrolic aldehyde may be prepared from corresponding acetals of alpha-chlorocrotonaldehyde, and acetals of higher alpha,beta-acetylenic aliphatic aldehydes may be prepared from the corresponding mono-halo olefinic acetals. Although for ordinary purposes it is desirable to employ the alpha-chloro olefinic aldehyde acetals, the process of the invention may be employed to convert the corresponding olefinic acetals in which there is an atom of a halogen other than chlorine attached to the olefinic carbon adjacent to the acetal grouping. Thus, in place of alpha-chloro-acrolein acetals, there may be employed acetals of alpha-bromoacrolein, of alpha-iodoacrolein, and even of alpha-fluroacrolein, and of homologous aliphatic alpha-halo-alpha,beta-olefinic aldehydes. The acetals may be those that would result from reaction of the free aldehyde with any suitable monohydric or polyhydric alcohol, although for ordinary purposes it usually is desirable to employ the acetals in which the acetal ether groups are alkoxy groups derived from a lower alkanol, such as methyl, ethyl, propyl, isopropyl, butyl, pentyl or like alcohols. Other acetals may be employed, however, such as acetals wherein the ethereal oxy groups are derived from aromatic alcohols, from polyhydric alcohols, or from cycloaliphatic alcohols, so it will be understood that in its generic concepts the invention is not to be construed as narrowly limited according to the particular acetals of the alpha-halo-alpha,beta-olefinic aldehydes of the hereindefined class.

We claim as our invention:

1. The method of preparing the dimethyl acetal of propargyl aldehyde which comprises heating a mixture of one part, by weight, of the dimethyl acetal of alpha-chloroacrolein with 3.3 parts of an aqueous solution of sodium hydroxide having a concentration of 15% by weight, at a temperature of 146° C. under a pressure of 77 pounds per square inch, and distilling the dimethyl acetal of propargyl aldehyde from the mixture at a rate substantially equal to its rate of formation therein.

2. The method of preparing the dimethyl acetal of propargyl aldehyde which comprises heating the dimethyl acetal of alpha-chloroacrolein with an excess of an aqueous solution of sodium hydroxide having a concentration from about 5% to about 30%, by weight, under a superatmospheric pressure from about 40 pounds per square inch to about 200 pounds per square inch at a temperature between about 130° C. and the temperature at which the total vapor pressure of the mixture equals the pressure that is employed.

3. The method of preparing the dimethyl acetal of propargyl aldehyde which comprises heating a mixture of the dimethyl acetal of alpha-chloroacrolein with an aqueous solution of a strong alkali having a concentration from about 5% to about 30% by weight, at a temperature from about 110° C. to about 220° C. under the autogenous pressure of the mixture.

4. The method of preparing the dimethyl acetal of propargyl aldehyde which comprises heating a mixture of the dimethyl acetal of alpha-chloroacrolein with an aqueous solution of a strong alkali having a concentration from about 5% to about 30% by weight, at a temperature from about 130° C. to about 170° C. under a superatmospheric pressure, and distilling the dimethyl acetal of propargyl aldehyde from the mixture at a rate substantially equal to its rate of formation therein.

5. The method of preparing a diacetal of propargyl aldehyde which comprises heating the corresponding diacetal of alpha-chloroacrolein in admixture with an aqueous solution of an alkali metal hydroxide having a concentration from about 2% to about 30% by weight, at a temperature from about 110° C. to about 220° C. under the autogenous pressure of the mixture.

6. The method according to claim 5 when the alkali metal hydroxide is sodium hydroxide.

7. The method of preparing a diacetal of propargyl aldehyde which comprises heating the corresponding diacetal of alpha-chloroacrolein in admixture with an aqueous solution of an alkali metal hydroxide having a concentration of from about 2% to about 30% by weight, under a superatmospheric pressure from about 40 pounds per square inch to about 200 pounds per square inch at a temperature between about 130° C. and the temperature at which the total vapor pressure of the mixture equals the pressure that is employed.

8. The method of preparing a diacetal of propargyl aldehyde which comprises treating the corresponding diacetal of alpha-chloroacrolein with an aqueous solution of a strong alkali at a dehydrohalogenation temperature, and distilling, as it is formed, the acetal of propargyl aldehyde from the reaction mixture.

9. The method of preparing a diacetal of an aliphatic alpha,beta-acetylenic aldehyde which comprises heating at a dehydrohalogenating temperature under a superatmospheric pressure a mixture of a diacetal of an aliphatic alpha-chloro-alpha,beta-olefinic aldehyde with an excess of an aqueous solution of a strong alkali having a concentration from about 2% to about 30% by weight.

10. The method of preparing an acetal of an aliphatic alpha,beta-acetylenic aldehyde which comprises treating a diacetal of an aliphatic alpha-halo-alpha,beta-olefinic aldehyde at a dehydrohalogenation temperature with an aqueous solution of a strong alkali.

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