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REARRANGEMENT OF UNSATURATED ALIPHATIC ALCOHOLS

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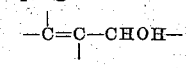
4 Claims. (Cl. 260—642)

This invention relates to a process for the rearrangement of unsaturated alcohols and relates more particularly to a process for rearranging aliphatic allyl type unsaturated primary alcohols to aliphatic allyl type unsaturated secondary alcohols and for rearranging aliphatic allyl type unsaturated secondary alcohols to aliphatic allyl type unsaturated primary alcohols.

The allylic or three-carbon type of rearrangement of aliphatic allyl type unsaturated alcohols such as crotyl alcohol, methyl vinyl carbinol and the like, has heretofore been considered extremely difficult if not impossible. In the production of these alcohols and products derived therefrom, there is great need for economical and efficient process for the conversion of a primary alcohol to the secondary alcohol isomer, a secondary alcohol to the primary alcohol isomer, or a secondary alcohol to a secondary alcohol isomer. This is particularly so where a process for the production of the unsaturated alcohol results in a product comprising a mixture of several isomers. Thus, crotyl chloride and methyl vinyl carbinyl chloride, the principal products of the high temperature chlor-substition of normal butylenes, rearrange on distillation at atmospheric pressure, or during hydrolysis, so that a mixture of the corresponding isomeric alcohols is always obtained. In order to produce substantially only the primary or only the secondary alcohol, some method for their controlled and efficient rearrangement is necessary. Such a method is provided by the present invention.

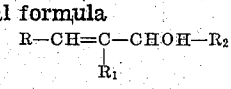
It is an object of the present invention to provide a novel, efficient and economical process for effecting the allylic rearrangement of an aliphatic allyl type unsaturated primary or secondary alcohol to an isomeric aliphatic allyl type unsaturated primary or secondary alcohol. The treatment of a primary unsaturated alcohol of the class to which the invention is applicable results in its rearrangement to the corresponding isomeric unsaturated secondary alcohol. Depending upon the structure of the particular alcohol treated, the treatment of an unsaturated secondary alcohol may result in its rearrangement to an isomeric primary alcohol or to a different isomeric secondary alcohol.

The aliphatic unsaturated alcohols which may be rearranged or isomerized in accordance with the process of the invention are characterized by possessing at least four carbon atoms in a chain two of which are joined by an olefinic linkage and one of which is a saturated primary or secondary carbon atom bearing a hydroxy group and directly linked to one of the unsaturated carbon atoms of the olefinic linkage. Such unsaturated alcohols are for purposes of convenience designated herein and in the appended claims as "allyl type alcohols," since they contain the grouping



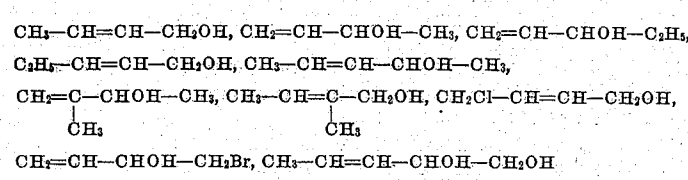
which is characteristic of allyl alcohol and its homologues.

The allyl type unsaturated alcohols to which the invention is applicable may be represented by the general formula



wherein R, R_1 and R_2 may represent hydrogen, alkyl radicals or substituted alkyl radicals but wherein at least R or R_2 represents an alkyl or substituted alkyl radical. The alkyl radicals which R, R_1 and R_2 may represent are, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, amyl, hexyl, etc. Representative substituted alkyl radicals which R, R_1 and R_2 may represent are the above-listed alkyl radicals and their homologues wherein one or more hydrogen atoms has been substituted by a suitable organic or inorganic substituent such as the halogen atoms, the hydroxy group, the carboxy group, the alkoxy groups and the like.

Specific allyl type unsaturated primary and secondary alcohols to which the process of the invention is applicable are, among others, the following:



and their homologues and suitable substitution products.

In accordance with the process of the invention the aliphatic unsaturated alcohol to be re-

arranged is heated in the presence of a suitable acidic rearranging medium while maintaining the hydrogen ion concentration of the rearranging medium within a prescribed optimum range. Suitable rearranging media consist of dilute solutions of a reagent capable of supplying a sufficiently high hydrogen ion concentration in a solvent having a high di-electric constant, for example, dilute aqueous solutions of inorganic acids such as sulfuric acid, hydrochloric acid, phosphoric acid, etc.

It has been found that by correlation of the concentration of the hydrogen ions in the rearranging medium the reaction temperature and the time of contact of the alcohol with the rearranging medium, undesirable side reactions can be reduced to a minimum and the desired isomeric alcohol prepared with excellent yields. The invention is described in detail with respect to its application to the preparation of crotyl alcohol from methyl vinyl carbinol and the preparation of methyl vinyl carbinol and the alcohol. It is to be understood, however, that the invention is not limited to the rearrangement of these specific unsaturated alcohols, but is applicable to all unsaturated primary and secondary alcohols of the class herein defined.

It has been found that crotyl alcohol can be rearranged to methyl vinyl carbinol and that methyl vinyl carbinol can be rearranged to crotyl alcohol as typified by the reversible equation:

$$CH_3 \cdot CH{=}CH \cdot CH_2OH \rightleftarrows CH_2{=}CH \cdot CHOH \cdot CH_3$$

with excellent yields and a minimum of undesirable side reactions by heating the alcohols at moderately elevated temperatures in a dilute aqueous acid solution and correlating the hydrogen ion concentration of the aqueous acid solution, and the time of contact of the alcohols with the acid solution.

The rearrangement of the alcohols is preferably effected in an aqueous medium but other solvents having a di-electric constant substantially as high as that of water may be used as the solvent for the acid. By heating crotyl alcohol with a 1% aqueous solution of sulfuric acid at atmospheric pressure and at a temperature of about 92° C., approximately equilibrium mixtures comprising about 70% methtyl vinyl carbinol and about 30% crotyl alcohol are obtained with a minimum formation of unsaturated ethers. The time of contact required to obtain a desired yield of isomeric alcohol may be substantially reduced by increasing the concentration of the acid in the rearranging medium. Increase in acid concentration, however, increases not only the rate of isomerization but undesired etherification, so that the use of acid solutions having a hydrogen ion concentration in excess of a well defined limited range will result in the formation of excessive undesirable reaction products. The use of even a trace of concentrated sulfuric acid as the rearranging medium results in the formation of products consisting of a mixture of unsaturated ethers with very little of the desired isomeric alcohol. On the other hand, aqueous solutions having too dilute a hydrogen ion concentration, for example, a 0.2% or less sulfuric acid solution, act extremely slowly producing but little of the desired isomeric alcohol. These extremely dilute solutions can, however, be used at higher temperatures and pressures. It is therefore essential that the hydrogen ion concentration of the rearranging medium be controlled within a well defined optimum range to obtain economically desirable yields of isomeric alcohols with a minimum of undesired reaction products.

In accordance with the process of the invention, the allyl type unsaturated alcohol to be rearranged is mixed with a suitable rearranging medium consisting of a dilute aqueous acid solution having a hydrogen ion concentration in terms of pH values of from 1.23 to 0.3. Although aqueous acid solutions having a hydrogen ion concentration as high as 0.3 in terms of pH values may suitably be used, it is preferred to carry out the process with aqueous acid solutions having a pH value in the range of 1.23 to 0.57 and still more preferably in the range of 0.95 to 0.75. For example, an aqueous 0.5% to 4%, preferably a 1% to 2.5%, sulfuric acid solution may be used.

Dilute aqueous sulfuric acid has been selected as a suitable rearranging medium in the description of the process of the invention. It is to be understood, however, that the invention is not limited to the use of this acid as a catalyst. Any suitable reagent capable of supplying a hydrogen ion concentration in terms of pH values of from about 1.23 to 0.3 in aqueous solution may be used. Inorganic acids, of which hydrochloric, hydrobromic, phosphoric, pyrophosphoric and dithionic are typical, may suitably be used in dilute aqueous solutions. Aqueous solutions or organic acids such as acetic acid, for example, work only slowly at atmospheric pressure but are more active, and may be used, if desired, at higher temperatures by working under superatmospheric pressures. Aqueous solutions of organic acids such as, for example, benzene sulfonic, naphthalene sulfonic, toluene sulfonic, their homologues and analogues may, however, suitably be used at atmospheric pressure. Good results have been obtained with the use of a 5% aqueous ethyl sulfonic acid solution as the rearranging medium in the rearrangement of crotyl alcohol to methyl vinyl carbinol. Suitable catalysts may also comprise solutions or suspensions of acid-acting salts such as, for example, sodium bisulfate, sodium bromide, sodium chloride, etc. in dilute aqueous solutions of suitable acids. Although the ratio of aqueous acid solution to alcohol may vary within a wide range within the scope of the invention, it is preferred to use a large excess of the aqueous acid solution. Thus, the ratio of aqueous acid solution to alcohol may be about 1 to 15 parts, preferably 8 to 12 parts, by volume of aqueous acid solution to 1 part by volume of alcohol to be rearranged. If desired, greater proportions of the dilute acid to alcohol may be used.

The mixture of alcohol and aqueous acid solution is heated in a suitable rearranging zone at a temperature sufficiently high to effect the desired degree of rearrangement but below that temperature at which substantial formation of undesirable reaction products is encountered. The temperature at which the mixture is heated will vary with the nature of the alcohols to be rearranged. The mixture may be heated at its boiling temperature at the operating pressure. In the rearrangement of crotyl alcohol and methyl vinyl carbinol excellent results have been obtained by heating the rearranging mixtures at about 96° C. and 92° C., respectively, at substantially atmospheric pressure. It is to be understood, however, that the rearrangement may be effected at temperatures substantially lower or substantially higher than the atmospheric boiling point of the mixture of alcohol and aqueous acid solution. Pressures in excess of atmospheric pressure may suitably be used to maintain all or a part of the

reactants in the liquid phase during the rearranging process. Any suitable type of still, fractionator, heating coil or the like, or a combination of any two or more of these, may be used as the rearranging zone.

Whatever the type of rearranging zone and operating conditions used, the time of contact of the alcohol and rearranging medium is controlled to obtain an optimum yield of the desired isomeric alcohol with a minimum of undesirable by-product formation and should preferably not exceed the minimum time required to attain equilibrium for a given dilute acid concentration. In the batchwise rearrangement of crotyl alcohol or methyl vinyl carbinol in an aqueous solution of 0.5% to 4% sulfuric acid at the atmospheric boiling temperature of the reaction mixture, the time of contact will be limited so as not to exceed, for example, a period of time increasing progressively with acid concentration used, from about 5 hours for a 0.5% acid concentration to about 40 minutes for a 4% acid concentration. Although batch or intermittent modes of operation may, if desired, be resorted to, it is preferred to carry out the process of the invention in any suitable continuous manner to reduce to a minimum the time of contact of the alcohols with the acid solution.

The alcohol to be rearranged may be charged in continuous stream into a still in vapor communication with a fractionating zone. A dilute aqueous acid solution, for example, a dilute sulfuric acid solution having a hydrogen ion concentration within the above-prescribed limits, is maintained within the still. The alcohol to be rearranged is introduced continuously into the acid solution at a rate which will assure the maintenance of a ratio of alcohol to acid solution within the prescribed limits. The liquid in the still is maintained at a temperature sufficiently high to effect the desired rearrangement and cause the passage of vapors comprising reaction products to an intermediate part of the fractionating zone. The desired isomeric alcohol is removed from the fractionating zone as a final product. Material comprising unconverted alcohol is returned continuously from the fractionator to the still.

The water azeotrope of methyl vinyl carbinol boils at 86.8° C. whereas the water azeotrope of crotyl alcohol boils at 94.2° C. Therefore, in rearranging either crotyl alcohol or methyl vinyl carbinol, the desired isomeric alcohol may be separated from the reaction mixture as the water azeotrope substantially as rapidly as it is formed therein. When the isomeric alcohol is removed from the rearranging zone as the water azeotrope, sufficient water is continuously added to the still to maintain the desired hydrogen ion concentration of the rearranging mixture.

It is to be understood that the invention is not limited in its application to processes to which but a single alcohol is charged. It is equally applicable to the processing of a mixture comprising, for example, two isomeric forms of a single alcohol to thereby obtain an increase in the proportion of the desired isomer in the resulting mixture or to convert all of one isomer to the corresponding isomeric form. The process of the invention is applicable, for example, to the rearrangement of 2 methyl butene-1-ol-3 and 2 methyl butene-2-ol-1.

$$CH_2{=}C(CH_3){\cdot}CHOH{\cdot}CH_3 \rightleftarrows CH_2OH{\cdot}C(CH_3){=}CH{\cdot}CH_3$$

which alcohols are obtained as a mixture by hydrolysis of the products obtained in the chlorination of tertiary amylene, and the conversion of which mixture to a product consisting of a single one of the two isomers by method available heretofore is difficult and uneconomical. The invention may also be applied to mixture comprising two or more homologues of an unsaturated alcohol, or comprising two or more entirely different unsaturated alcohols, capable of undergoing rearrangement, to thereby obtain a desired mixture containing an increased proportion of desired isomers.

Example I

About 50 parts by volume of crotyl alcohol were mixed with about 500 parts by volume of a 1% aqueous sulfuric acid solution and the mixture heated at a temperature of 95.5° C. for approximately 5 hours in a still provided with a reflux condenser returning all condensate to the still. The mol per cent composition of the alcohols and ethers in the reaction products is given in column A.

About 50 parts by volume of crotyl alcohol were mixed with about 500 parts by volume of a 4% aqueous sulfuric acid solution and the mixture was heated under identical conditions for about ½ hour. The mol per cent composition of the alcohols and ethers separated from the reaction products is given in column B.

	A	B
Methyl vinyl carbinol	61.1	56.3
Crotyl alcohol	33.5	38.0
Ethers	5.4	5.7

Example II

About 50 parts by volume of methyl vinyl carbinol were mixed with about 500 parts by volume of a 1% aqueous sulfuric acid solution and heated at a temperature of 92° C. for approximately 5 hours in a still equipped with a reflux condenser returning all condensate to the still. The mol per cent composition of the alcohols and ethers separated from the reaction products was found to be as follows:

Crotyl alcohol	24.7
Methyl vinyl carbinol	71.0
Ethers	4.3

Example III

An initial charge consisting of 2.1 liters of a mixture of 1% aqueous sulfuric acid and crotyl alcohol in the proportion of 0.556 mol of crotyl alcohol per liter of aqueous sulfuric acid was heated in a still provided with a reflux condenser. The liquid in the still was maintained at a temperature of 95.5° C. and the stillhead at about 89° C. The methyl vinyl carbinol formed was removed as rapidly as formed overhead from the fractionator as the water azeotrope containing 24.8% water. Crotyl alcohol was continuously added to the flask to maintain the concentration of 0.556 mol of crotyl alcohol per liter of aqueous acid. A total of 2.655 mols of crotyl alcohol were added continuously to the liquid in the flask during the course of the operation. Water was continuously introduced into the flask to replace the water removed in the water azeotrope of methyl vinyl carbinol.

Upon terminating the operation there remained 0.903 mol of unconverted alcohol in the flask. 2.63 mols of methyl vinyl carbinol were separated from the azeotrope removed overhead from the

fractionator. Less than 4% of the crotyl alcohol charged was converted to ethers and only traces of glycols were formed.

We claim as our invention:

1. A process for rearranging crotyl alcohol to methyl vinyl carbinol which comprises heating crotyl alcohol with an aqueous solution of 1% to 2.5% sulfuric acid at about the atmospheric boiling temperature of the reaction mixture, and continuously distilling methyl vinyl carbinol from the reaction mixture substantially as soon as it is formed therein.

2. A process for rearranging crotyl alcohol to methyl vinyl carbinol which comprises heating crotyl alcohol with an aqueous solution of 0.5% to 4% sulfuric acid, and continuously distilling methyl vinyl carbinol from the reaction mixture substantially as soon as it is formed therein.

3. A process for effecting the rearrangement of crotyl alcohol to methyl vinyl carbinol which comprises heating crotyl alcohol with an aqueous acid solution having a pH of from 1.23 to 0.57, and continuously distilling methyl vinyl carbinol from the reaction mixture substantially as soon as it is formed therein.

4. A process for effecting the rearrangement of an aliphatic unsaturated primary monohydric alcohol containing at least four carbon atoms and an olefinic linkage between two carbon atoms, one of which is directly linked to the primary carbinol group, to an isomeric aliphatic unsaturated secondary alcohol containing an olefinic linkage between two carbon atoms, one of which is linked directly to a secondary carbinol group, which comprises heating the unsaturated primary alcohol with an aqueous acid solution having a pH of from 1.23 to 0.57, and continuously distilling the isomeric unsaturated secondary monohydric alcohol from the reaction mixture substantially as soon as it is formed therein.

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