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PREPARATION OF 1,5-PENTANEDIOLS

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This invention relates to a method for the preparation of 1,5-diols, and more particularly relates to a method for the production of 1,5-diols, by the simultaneous treatment with hydrogen and an aqueous medium, of compounds in the dihydropyran series of compounds to produce in unusually high yields 1,5-diols such as are exemplified by 1,5-pentanediol (pentamethylene glycol).

The process of the invention has as one of its objects a method for the preparation of 1,5-diols, particularly 1,5-pentanediol.

Another object of the invention is a single-step process for the preparation of such diols from compounds in the dihydropyran series of compounds.

A still further important object of the invention is a method to prepare such diols, in particular 1,5-pentanediol, in high yields and with a minimum of manipulative steps.

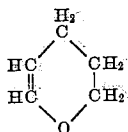
An additional object of the invention is to prepare 1,5-diols from compounds in the dihydropyran series of compounds in high yields and with a maximum of efficiency in operation.

An ancillary object of the invention is a process that may be carried out, as in commercial operation of the process, by one not skilled in the art, e. g., a chemically untrained operator, with minimum danger of unsuccessful outcome arising from lack of precise control by the operator or from lack of chemical skill on the part of the operator.

A more specific object of the invention is an improved process for the preparation of 1,5-diols, particularly 1,5-pentanediol, from compounds in the dihydropyran series of compounds.

Other related objects of the invention will become apparent as the invention is more particularly described hereinafter.

It has been proposed (see Bull. soc. chim. [5] 1, 971 (1934)) to prepare 1,5-pentanediol by treating dihydropyran-1,4.



with N/70 aqueous hydrochloric acid at reflux temperature, and reducing the resultant product, after neutralization of the acid, by treatment with mercury-aluminum amalgam. Such a process requires the three distinct steps of (a) hydrolyzing the dihydropyran-1,4, (b) neutralizing the intermediate product, and (c) reducing

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the intermediate product. Furthermore, the process as described in the literature led to undesirably low yields (ca. 50%) of the desired product, and also involved consumption of the rather expensive amalgam.

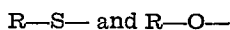
An improvement on the foregoing known process has been proposed (see J. Am. Chem. Soc., 68, 1646 (1946)) which comprises hydrolyzing the dihydropyran, carefully neutralizing the resultant mixture, isolating the intermediate product that was formed by hydrolysis, and hydrogenating the isolated intermediate product by treatment with hydrogen gas under a pressure of 2000 pounds per square inch and at 150° C. in the presence of copper-chromite hydrogenation catalyst. Although a certain improvement in yield over the previously known process was disclosed, it was found that attempts to carry out the process without the intermediate isolation of the product of the hydrolysis resulted in a substantial reduction in the yields that were obtained. It also was found that the accuracy with which the acid in the hydrolysis mixture was neutralized prior to distillation of the mixture was an important factor in determining the yields that were obtained, failure to carefully neutralize the acid leading to substantially reduced yields of the desired 1,5-pentanediol. Therefore, this latter process, while representing an advance over the first-mentioned known process, was not entirely satisfactory because (a) it required the several steps enumerated immediately above (b) each additional step would require additional apparatus and/or additional working time, (c) the process would require the skillful manipulation of the intermediate mixtures in order to obtain optimum yields of the desired product and (d) even under the optimum conditions as disclosed, the yields of the desired product that were obtained were not as high as could be desired. While for laboratory purposes a process having these features might not be highly objectionable, such features could impair significantly the usefulness and value of a process for application on a scale of commercial operations because of the expense of the equipment and skilled operator's time that would be required and because of the careful control with which the neutralization step of the process would have to be carried out to avoid undesirable reduction in the yield of the desired product.

In the attainment of its objects, the present invention has overcome the difficulties that thus are associated with the prior art process and in so doing has provided a process whereby 1,5-

diols may be prepared in a single step from compounds in the dihydropyran series of compounds, without reduced yields compared to the yields that are obtained in a process, such as the above prior art processes, that comprise a plurality of steps. The present process may be executed under conditions which may be maintained within relatively wide limits and without the necessity for precise control or skillful manipulation that are required for the attainment of optimum yields according to the prior art methods. As a consequence, the process of the present invention is better suited to application on a commercial scale than are the mentioned prior art processes. Furthermore, the process of the invention has provided an improvement over the prior art methods of preparing 1,5-diols from compounds in that there may be obtained, despite the single step character of the process, yields of the desired product substantially greater than the yields that heretofore have been attained.

Broadly stated, the process of the present invention comprises hydrolyzing in the presence of a hydrogenation catalyst and of hydrogen under conditions which favor hydrogenation reaction, a substituted 3,4-dihydro-1,2-pyran containing an organic substituent group attached by a hydrolyzable bond to the carbon atom in the No. 2 position of the dihydropyran ring through a divalent atom of a non-metallic element of group VI of the periodic table of the elements. It has been discovered in accordance with the present invention that by subjecting to simultaneous hydrolysis and hydrogenation derivatives of 3,4-dihydro-1,2-pyran which contain an organic substituent group that may be removed, or split-off, by hydrolysis attached to the carbon atom in the No. 2 position of the dihydropyran ring through a divalent atom of a non-metallic element of group VI of the periodic table of the elements, there may be obtained 1,5-diols in yields that are at least equal to the yields that the obtained by successively hydrolyzing the same derivative of dihydropyran, isolating the hydrolysis products, and hydrogenating the isolated products of the hydrolysis. The results that are thus provided by the invention are critically dependent upon the presence in the 2-position of the dihydropyran ring of such a substituent group that may be removed, or split-off, by hydrolysis, since attempts to simultaneously hydrolyze and hydrogenate 3,4-dihydro-1,2-pyran or a derivative thereof which does not contain at the No. 2 position a substituent group of the above defined character, lead to yields substantially below the yields that are obtained by successively carrying out the enumerated steps.

If, in the following formulas, R represents the 2-(3,4-dihydro-1,2-pyranyl) group or a substituted 2-(3,4-dihydro-1,2-pyranyl) group, the derivatives of dihydropyran which preferably may be employed in the execution of the process of the present invention may be represented by the structural formulas

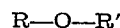


in which the free valencies at the O and S atoms, respectively, are satisfied by organic groups which preferably are bonded to the indicated free valencies at an atom of carbon. In most cases the desired 1,5-diol is derived solely from the carbon atoms of the 2-(3,4-dihydro-1,2-pyranyl) group or the substituted 2-(3,4-di-

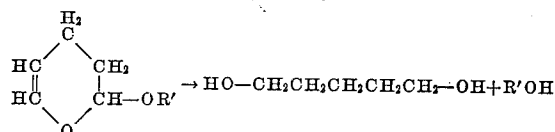
hydro-1,2-pyranyl) group represented by R. The carbon atom or atoms of the organic group that is attached to the free valency of the S or the O atom in the above formulas ordinarily do not form a part of the desired product. (The exception to the general rules arises in certain cases in which an additional amount of the diol may be derived from the said organic group. It will be apparent, therefore, that the exception does not limit the following sentence, but, instead, is an exception only to the generalities described in the two sentences immediately preceding). From the standpoint of operability in the presence of the invention, the substituted dihydropyran therefore may be one which contains any of a wide variety of substituent groups attached by a hydrolyzable bond to the carbon atom in position No. 2 of the dihydropyran ring through a divalent atom of oxygen or sulfur. Illustrative of the substituted 3,4-dihydro-1,2-pyrans which may be employed in the execution of the process of the invention are included, among others, those which have the following exemplary groups attached to the carbon atom in the No. 2 position of the dihydropyran ring: OR' , SR' , $-O-OC-R'$, $-O-SC-R'$, $-S-OC-R'$, $-S-SC-R'$, etc., in which R' represents an unsubstituted or a substituted hydrocarbon group.

Additional substituent groups, such as one or more hydrocarbon groups, may be attached to carbon atoms in the dihydropyran ring, such hydrocarbon groups, if present, preferably being non-reactive to hydrogen under the conditions under which the process is executed, e. g., hydrocarbon groups containing only saturated or aromatic carbon-to-carbon bonds, such as alkyl, cycloalkyl, aryl, alkaryl, aralkyl, and like groups.

A preferred group of derivatives of 3,4-dihydro-1,2-pyran which may be employed in the execution of the process of the present invention comprises those derivatives which have structures that may be represented by the formula

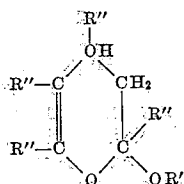


in which R signifies the 2-(3,4-dihydro-1,2-pyranyl) group or a substituted 2-(3,4-dihydro-1,2-pyranyl) group and R' signifies a hydrocarbon group. It has been discovered that because of advantages with which they may be prepared and their suitability to the objects of the invention, the foregoing derivatives of 3,4-dihydro-1,2-pyran are particularly desirable for use in the process of the invention. Furthermore, compounds corresponding in structure to the above formula may be employed to produce with particular and outstanding efficacy and in particularly high yields, 1,5-diols which are desired in accordance with the invention. The over-all reaction which is caused to take place by the process of the invention may be exemplified, but not limited in the scope of its applicability, by the preparation of 1,5-pentanediol from a derivative of 3,4-dihydro-1,2-pyran having the above structure when R signifies the unsubstituted 2-(3,4-dihydro-1,2-pyranyl) group, as follows:



It will be noted that in this equation the group represented by R' does not form a part of the desired product. The specific identity of the

hydrocarbon group R' therefore is not a critical factor in determining the successful outcome of the process and, in fact, the hydrocarbon group represented by R' may be almost any hydrocarbon group, and may be saturated or unsaturated, acyclic or cyclic, aromatic or non-aromatic, unsubstituted or substituted. It is preferred that the group R' be relatively non-reactive with hydrogen, i. e., a saturated or an aromatic group such as an alkyl, aryl, aralkyl, alkaryl, cycloalkyl, or like group, since unnecessary saturation of unsaturated carbon-to-carbon linkages in the group R' otherwise may occur during the execution of the process. It is particularly desirable that the group R' be such that the hydroxylic compound R'OH is miscible with water, e. g., a lower alkyl group, although the invention is not to be construed as thus limited in its more generic aspects. Representative hydrocarbon groups which may be represented by R' include, for example, phenyl, tolyl, xylyl, phenethyl, cyclohexyl, cyclopentyl, methylcyclopentyl, ethylcyclohexyl, heptyl, octyl, decyl, stearyl, phenylhexyl, tolylbutyl, and homologous and analogous groups; less desirably groups containing one or more non-aromatic unsaturated carbon-to-carbon bonds, such as vinyl, allyl, methallyl, cyclohexenyl, crotyl, cinnamyl, and the like, and most desirably the lower alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, and their branched-chain analogs. A preferred group of derivatives of dihydropyran which may be employed in the execution of the process of the invention has the formula



in which R' has its above significance and each R'' represents a hydrogen atom or a hydrocarbon group, preferably a hydrocarbon group which is relatively resistant to hydrogenation, such as an alkyl, aryl, alkaryl, aralkyl, cycloalkyl group, or the like. The completely aliphatic 1,5-diols, i. e., the 1,5-alkanediols, are particularly valuable products for certain applications in the arts. For the preparation of 1,5-alkanediols, we may employ derivatives of dihydropyran corresponding to the last-given formula when each R'' represents a hydrogen atom or an alkyl group, preferably one containing from 1 to about 10 carbon atoms.

Illustrative derivatives of dihydropyran which may be employed in the process of the present invention may be illustrated by the following non-limiting group of compounds: 2-(3,4-dihydro-1,2-pyran-1-yl) methyl ether, 2-(3,4-dihydro-1,2-pyran-1-yl) ethyl ether, 2-(3,4-dihydro-1,2-pyran-1-yl) propyl ether, 2-(4-methyl-3,4-dihydro-1,2-pyran-1-yl) isopropyl ether, 2-(5-methyl-3,4-dihydro-1,2-pyran-1-yl) butyl ether, 2-(5-butyl-3,4-dihydro-1,2-pyran-1-yl) isobutyl ether, 2-(2-methyl-3,4-dihydro-1,2-pyran-1-yl) isopropyl ether, 2-(2,4-dimethyl-3,4-dihydro-1,2-pyran-1-yl) methyl ether, 2-(4-cyclohexyl-5-methyl-3,4-dihydro-1,2-pyran-1-yl) ethyl ether, 2-(5-phenyl-3,4-dihydro-1,2-pyran-1-yl) isobutyl ether, 2-(6-methyl-3,4-dihydro-1,2-pyran-1-yl) methyl ether, 2-(5-octyl-3,4-dihydro-1,2-pyran-1-yl) propyl ether, 2-(5-phenethyl-6-methyl-3,4-dihydro-1,2-pyran-1-yl) pentyl ether and analogous and homologous compounds.

According to one embodiment of the invention, the compound R—O—R' may be symmetrical, i. e., R and R' both may represent 2-(3,4-dihydro-1,2-pyran-1-yl) groups or substitution products thereof. In this embodiment of the invention, the formation of the by-product alcohol R'OH is avoided, both of the groups R and R' reacting to form a diol of the desired type with consequent 100% efficiency of the process with respect to the carbon balance between the organic reactant and the desired product.

Derivatives of 3,4-dihydro-1,2-pyran which may be employed in the process of the invention may be prepared conveniently and economically according to the method disclosed and claimed in the copending application, Serial No. 751,980, filed June 2, 1947, now Patent No. 2,514,168. According to the method of the copending application, an alpha,beta-olefinic aldehyde, such as acrolein or a substituted acrolein containing an alkyl, aryl, alkaryl, or aralkyl group attached to either or to each of the alpha and the beta carbon atoms, may be reacted with a vinyl compound CH₂=CH—OR', in which R' has its hereinabove significance, at an elevated temperature under conditions which substantially minimize polymerization of the reactants, to prepare directly and in a single step the above derivatives of 3,4-dihydro-1,2-pyran which advantageously may be utilized in the present process. The method of the aforesaid copending application may be practiced by heating a mixture of the alpha,beta-olefinic aldehyde and the said vinyl compound present in about equimolar proportions containing an amount of a polymerization inhibitor, such as hydroquinone, sufficient to substantially minimize polymerization, to a temperature of about 150° C. to about 225° C. under an elevated pressure sufficient to maintain the reaction mixture in the liquid state. Reaction times of from about 1/2 to about 2 hours may be employed. After the reaction, the desired product formed thereby may be separated from the reaction mixture prior to its use in the present process, or in some cases the entire reaction mixture in its crude form may be employed for the preparation of 1,5-diols according to the process of the present invention.

The process of the present invention may be carried out by hydrogenating in the presence of an aqueous medium and a hydrogenation catalyst under conditions of elevated temperature and superatmospheric pressures of hydrogen conducive to hydrogenation reaction, a derivative of 3,4-dihydro-1,2-pyran of the herein defined character. As the hydrogenation catalyst there may be employed any suitable metal or compound of a metal of the type well-known and customarily referred to in the art as hydrogenation catalysts. It is desirable to employ as the hydrogenation catalyst a metal or a compound of a metal which may be easily and economically prepared, which has a high degree of activity, and which retains its activity under the conditions of the process for a length of time sufficient to avoid the necessity of reactivating or replacing the catalyst at too frequent intervals. Generally speaking, hydrogenation catalysts which may be employed in the execution of the process of the invention include the metal hydrogenation catalysts, such as Pt, Pd, Au, Ag, Cu, V, W, Co, Ni, Ru, Rh, Mn, Cr, Mo, Ir, Os, Pb, and the like and mixtures of the same and compounds and alloys thereof, particularly oxides and sulfides thereof, and like hydrogenation catalysts. Because of the ease and

economy with which they may be prepared, and because of their characteristics which render them particularly suited to the objects of the invention in the way of providing high yields of the desired product and their lack of tendency to promote undesired side reactions, the base metal hydrogenation catalysts, particularly the pyrophoric base metal hydrogenation catalysts such as nickel, cobalt, and iron, are preferred. Because of its availability and its particular efficacy when employed in the process of the invention, the well-known nickel hydrogenation catalyst customarily referred to in the art as Raney nickel hydrogenation catalyst is a preferred catalyst. The hydrogenation catalyst may be employed in a finely divided form and dispersed in and throughout the reaction mixture, or it may be employed in a more massive state, either in essentially the pure state or supported upon or carried by an inert or catalytically active supporting or carrier material, such as pumice, kieselguhr, diatomaceous earth, clay, alumina, charcoal, carbon, or the like, and the reaction mixture contacted therewith as by flowing the mixture over or through a bed of the catalyst or according to other methods that are known in the art.

If desired the process of the present invention may be executed in the presence of a suitable acid-reacting material which serves to acidify the aqueous medium and thereby increase to a certain extent the reaction rate under the otherwise existing reaction conditions. In large scale applications of the process, it frequently may be advantageous to carry out the process employing a non-alkaline aqueous medium that contains a minimum of added acid-reaction materials, thereby avoiding or minimizing any additional steps that would be required for the purpose of separating the acid catalyst from the reaction mixture as a part of the treatment leading to recovery of the desired product. If an acidic catalyst is employed, any suitable acid-reacting material may be used, such as a strong mineral acid, an acid-reacting salt, or a material which will react under the conditions of the process to form in situ an acid-reacting material. The acid-reacting material must be one that does not adversely affect the hydrogenation catalyst, i. e., it must be non-poisonous to the hydrogenation catalyst. Suitable acid-reacting materials which may be employed to increase the reaction rate include, for example, mineral acids, such as HCl, H₂SO₄, HBr, HI, H₃PO₄, H₄P₂O₇, HNO₃, H₂SeO₄, H₂SO₃ and the like; acid-reacting salts, such as NaHSO₄, NaH₂PO₄, KH₂PO₄, ZnCl₂, MgCl₂, ZnSO₄, FeCl₃, Al₂(SO₄)₃, and the like. There also may be employed compounds which form mineral acids with water, such as SO₂Cl₂, SOCl₂, N₂O₃, PCl₃, PCl₅, and the like. As the acidifying agent there also may be employed suitable organic acids, particularly the water-soluble organic acids, such as the lower aliphatic carboxylic acids, halogenated aliphatic carboxylic acids, dibasic carboxylic acids, aromatic acids, and the like. It is not necessary that the acid-reacting catalyst be infinitely soluble in water, since it is necessary only that amounts sufficient to influence the reaction rate be present in the dissolved state. Therefore, organic acids that are less soluble in water, than those just mentioned also may be employed as the acidifying agent if desired, including, for example, aromatic sulfonic acids, higher, less-soluble aliphatic carboxylic acids, dialkyl and alkyl sulfates, alkylated phosphoric acids, and the like. Because of their freedom

from any tendency to poison the hydrogenation catalysts that may be employed in the execution of the process of the invention, the lower fatty acids, such as the lower fatty acids containing from one to about four carbon atoms are particularly effective for use in the process of the invention. It is desirable, if an acid catalyst is employed, to use one that is easily separated from the reaction mixture after completion of the desired reaction, or, alternatively, one from which the desired product may be easily separated. The volatile organic acids, such as the lower aliphatic monocarboxylic acids are advantageous in this respect because they generally may be conveniently separated from the desired product as by fractional distillation of the reaction mixture. Mineral acids such as sulfuric acid, hydrochloric acid, or the like, may be removed from the reaction mixture after completion of the reaction by addition of a suitable base or basic salt which forms a water-insoluble of lime or calcium carbonate or of baria, hydrochloric acid may be neutralized by the addition of silver oxide, etc., and the resulting insoluble salt may be removed by filtration or in other ways that will be apparent to those skilled in the art.

The amount of the acidifying agent, if one is employed, may be varied over relatively wide limits. Strong mineral acids and acid-reacting substances of equivalent acidic strength may be employed in amounts of from about 0.00005 to 1 or more acid-equivalents per liter of water, amounts not over about 0.2 acid-equivalent per liter of water being preferred. Amounts of acetic acid and weak acids of equivalent acidic strength up to about 5% by weight, based on the weight of the water, have been found to provide highly favorable results. More broadly speaking, amounts of the acid-reacting material from 0 up to about 40% by weight of the water that is present may be employed. When the acid catalyst is one that must be removed, as by neutralization, prior to recovery of the desired product, it usually is desirable to employ only small amounts in order to minimize the consumption of acid in the process. Those acids which can be recovered as such from the reaction mixture, i. e., without neutralization, usually may be employed in somewhat larger amounts without uneconomic consumption of acid. Because of the possibility that the presence of excessive amounts of an acid or acid-reacting material would affect adversely the activity of the hydrogenation catalyst, it is particularly preferred to employ from about 0% to about 2% by weight of the acidifying agent, based on the weight of the water that is present.

The process of the invention may be executed effectively when water (i. e., distilled or tap water) is employed as the aqueous medium. However, the invention also includes the addition to the aqueous medium of substances which facilitate the reaction as by their physical effect in the reaction mixture. For example, if it is desired to render the derivative of dihydropyran more miscible with the aqueous medium in those instances in which the two are highly immiscible, mutual solvents, such as lower alcohols, heterocyclic oxygen-containing solvents, glycols containing, for example, from 2 to 3 carbon atoms, and the like, may be included in the mixture. Although their presence is not essential to the successful execution of the process of the invention, such additional materials may desirably facilitate the carrying out of the process, pos-

sibly through their effect upon the physical characteristics of the reaction mixture.

The amount of the aqueous medium that is employed desirably contains a quantity of water at least equimolar to the amount of the substituted 3,4-dihydro-1,2-pyran, it being preferred to employ amounts of water in excess of about 1.5 moles per mole of the substituted 3,4-dihydro-1,2-pyran. There is no known theoretical maximum to the amount of the water that may be present, although for practical reasons it is desirable to maintain the amount within reasonable limits. In order to avoid excessive dilution of the reaction mixture, with consequent reduction in the effectiveness of the contact between the organic reactant and the hydrogenation catalyst, it is desirable to employ not over about 100 moles of water per mole of the substituted 3,4-dihydro-1,2-pyran, a preferred maximum being about 10 moles of water per mole of substituted 3,4-dihydro-1,2-pyran.

The process of the invention may be executed by treating a mixture of the substituted 3,4-dihydro-1,2-pyran and the aqueous medium in the presence of the hydrogenation catalyst with hydrogen or a hydrogen-containing gas at an elevated temperature and under superatmospheric pressure of hydrogen until the absorption of hydrogen is essentially complete, and recovering from the mixture the 1,5-diol that thereby is formed. Broadly speaking, temperatures of from about 50° C. to about 350° C. may be employed. A preferred range of temperatures comprises temperatures at which the reaction proceeds at a rate most suited to practical application of the process while avoiding the possibility of excessive side reactions which could occur at excessively elevated temperatures and comprises temperatures within the range of from about 100° C. to about 250° C. Hydrogen pressures greater than about 250 pounds per square inch are effective for accomplishing the objects of the invention. The maximum pressure of hydrogen that may be employed is determined largely by the strength of the equipment that is used, and is not known to be critical. A convenient maximum pressure of hydrogen is 10,000 pounds per square inch, and a preferred range of hydrogen pressures is from about 1000 to about 5000 pounds per square inch.

The process of the present invention may be executed in any suitable manner and in any suitable apparatus of the type that is customarily employed for hydrogenation processes. A method of carrying out the process which has been found to be advantageous comprises mixing the substituted 3,4-dihydro-1,2-pyran with the aqueous medium in a pressure-resistant vessel equipped with the necessary inlets and outlets, heating means, pressure gauge thermometer, etc., and desirably with means for agitating the contents, and subjecting the mixture to the action of hydrogen gas under the aforesaid conditions of temperature and pressure in the presence of the hydrogenation catalyst until absorption of hydrogen is for practical purposes complete. Instead of in a batchwise method, the process may be carried out in an intermittent or continuous manner, as by flowing a stream of a mixture comprising the aqueous medium and the substituted 3,4-dihydro-1,2-pyran over and/or through a fixed or moving bed of the hydrogenation catalyst under an atmosphere of hydrogen and at conditions of temperature and pressure of hydrogen as aforesaid. There is produced, as the

direct result of the treatment with hydrogen of the mixture of the aqueous medium and the substituted 3,4-dihydro-1,2-pyran, the 1,5-diol that is desired as the ultimate product of the process, steps such as those involving separation of an intermediate reaction product, or adjustment or manipulation of an intermediate reaction mixture, being avoided. At the conclusion of the hydrogenation treatment, the desired product therefore may be recovered directly from the reaction mixture in any suitable manner. For example, the hydrogenation catalyst, if dispersed in the reaction mixture, may be removed by filtration, centrifugation, or by other means which will be apparent to those skilled in the art. If an acidifying agent is present and its continued presence during the recovery treatment would be objectionable, it may be removed at this time, illustrative suitable methods for its removal having been referred to hereinbefore. The desired 1,5-diol may be further purified in any suitable manner, such as by evaporation or distillation of the more volatile components of the remaining mixture, by fractional distillation, by treatment with selective solvents, by crystallization, or according to other possible methods that will be known to those skilled in the art.

The following examples will illustrate certain of the possible specific embodiments of the invention. It will be appreciated that the examples are presented for the purpose of illustrating the invention and not to unnecessarily limit the same as it is defined in the appended claims. It also will be understood that we do not intend to limit the invention, other than as it is defined in the appended claims, according to any theories, expressed or implied, that may have been referred to during the discussion of the invention. In the examples, the parts are by weight.

Example I

One thousand parts of 2-(3,4-dihydro-1,2-pyran-1-yl) methyl ether and 316 parts of water were mixed in a pressure-resistant reaction vessel suitable for hydrogenation processes. The vessel was constructed of S. A. E. 4140 hydrogenation steel and was equipped with the customary thermometer for measuring the temperature of the contents, a pressure gauge, a stirrer, and internally located heating coils through which steam could be passed, and was provided with an inlet for hydrogen, etc. To the mixture there were added 65 parts of Raney nickel hydrogenation catalyst. The vessel was closed from the atmosphere and air remaining in the vessel was washed out with hydrogen gas. Hydrogen under pressure was introduced into the vessel, and the contents were heated with agitation to 150° C. under a hydrogen pressure of 1500 pounds per square inch. After four hours, the pressure was released, and the reaction mixture was taken from the reaction vessel and filtered to remove the hydrogenation catalyst. The filtrate was fractionally distilled to recover 1,5-pentanediol. In this experiment, the 1,5-pentanediol was recovered in a yield of 95% based on the amount of the dihydropyran-1-yl methyl ether consumed, and in a conversion of 90% based on the amount of dihydropyran-1-yl methyl ether employed, as a fraction distilling from 103° C. to 108° C. under a pressure of 1 mm. Hg. The above yield figure takes credit for a small amount of a mixture of intermediate products that was separated as a forecut during the distillation. By the use of slightly more rigorous conditions during the hy-

drogenation or by re-passing it through the process with a further batch of the reaction mixture, the forecut would have been converted to 1,5-pentanediol, since hydrogenation of the forecut completely converted the intermediate materials in it to 1,5-pentanediol.

Example II

A mixture of 510 parts of 2-(4-methyl-3,4-dihydro-1,2-pyran-1-yl) methyl ether, 250 parts of water, 200 parts of methyl alcohol, and 2 parts of glacial acetic acid was placed in the reaction vessel that was employed in Example I. One hundred parts of Raney nickel hydrogenation catalyst were added to the mixture. The mixture was subjected to the action of hydrogen, with agitation, at a temperature of 150° C. and a hydrogen pressure of 1300 pounds per square inch for two hours. The mixture then was taken from the reaction vessel and filtered to remove the hydrogenation catalyst. The filtrate was fractionally distilled. After distillation of water and methanol, 3-methyl-1,5-pentanediol was separated as a fraction distilling from 84° to 95° C. under a pressure of 0.7 mm. Hg in the amount of 320 parts, corresponding to a yield of 71.5% based on the amount of the methyldihydropyran-1-yl methyl ether that was consumed.

Example III

A mixture of 560 parts of 2-(5-methyl-3,4-dihydro-1,2-pyran-1-yl) n-butyl ether, 500 parts of water, and 2 parts of glacial acetic acid was prepared and placed in the reaction vessel that was used in the foregoing examples. One hundred parts of Raney nickel hydrogenation catalyst were added to the mixture and the mixture was exposed, with agitation, at a temperature of 150° C. for 16 hours to hydrogen gas under a pressure of 1200 pounds per square inch. The mixture then was taken from the reaction vessel, the hydrogenation catalyst was removed by filtration, and the filtrate was fractionally distilled under reduced pressure. After removal of water and n-butanol, 2-methyl-1,5-pentanediol was recovered as the fraction distilling between 80° C. and 89° C. in an amount corresponding to 265 parts. Redistillation of the 2-methyl-1,5-pentanediol gave a heart cut with the following properties: Boiling point, 89° C.; refractive index n_D^{20} , 1.4532; specific gravity (20/4), 0.9724.

Example IV

Eleven hundred forty parts of 2-(3,4-dihydro-1,2-pyran-1-yl) methyl ether, 360 parts of water, and 1 part of glacial acetic acid were mixed in the reaction vessel that was employed in Example I. To the mixture was added 150 parts of Raney nickel hydrogenation catalyst. Air was displaced from the vessel by introduction of hydrogen, the vessel was closed from the atmosphere and the hydrogen pressure was increased to 1500 pounds per square inch. The temperature of the vessel and its contents was raised to 150° C. and kept at this value for 4 hours. During this time the contents of the vessel were agitated. The vessel then was cooled and the pressure released, and the contents of the vessel were withdrawn. After removal of the hydrogenation catalyst by filtration, the mixture was fractionally distilled. 1,5-pentanediol was recovered in a conversion of 92% based on the amount of 2-(3,4-dihydro-1,2-pyran-1-yl) methyl ether employed.

Example V

A mixture of 1140 parts of 2-(3,4-dihydro-1,2-pyran-1-yl) methyl ether, 1100 parts water, and 200 parts Raney nickel hydrogenation catalyst was subjected according to the method of the preceding examples at 150° C. for 3 hours to the action of hydrogen gas under a pressure of 1500 pounds per square inch. After removal of the hydrogenation catalyst by filtration, the resultant mixture was fractionally distilled. 1,5-pentanediol was recovered in a conversion of 90% based on the amount of 2-(3,4-dihydro-1,2-pyran-1-yl) methyl ether employed.

I claim as my invention:

1. The method of producing 1,5-pentanediol consisting in hydrogenating at a temperature from about 100° C. to about 250° C. under a pressure of hydrogen from about 1000 to about 5000 pounds per square inch in the presence of Raney nickel hydrogenation catalyst, a mixture comprising a 2-(3,4-dihydro-1,2-pyran-1-yl) lower alkyl ether and from about 1.5 to about 10 molar equivalents of acidulated water.

2. The method of producing 1,5-pentanediol consisting in hydrogenating at a temperature from about 50° C. to about 350° C. under a pressure of hydrogen from about 250 to about 10,000 pounds per square inch, in the presence of a hydrogenation catalyst, a mixture comprising 2-(3,4-dihydro-1,2-pyran-1-yl) lower alkyl ether and water in an amount at least molecularly equivalent thereto.

3. The method of producing 1,5-pentanediol consisting in hydrogenating at a temperature from about 50° C. to about 350° C. under a pressure of hydrogen from about 250 to about 10,000 pounds per square inch, in the presence of a hydrogenation catalyst, a mixture comprising a 2-(3,4-dihydro-1,2-pyran-1-yl) organic ether wherein the dihydropyran-1-yl group is unsubstituted and water in an amount at least molecularly equivalent thereto.

4. The method of producing 1,5-diols consisting in hydrogenating in the presence of a hydrogenation catalyst under conditions of an elevated temperature and a superatmospheric pressure of hydrogen conducive to hydrogenation reaction, a mixture comprising a 3,4-dihydro-1,2-pyran having an organic substituent group attached to the carbon atom in position No. 2 of the dihydropyran ring by a hydrolyzable bond to a divalent atom of a non-metallic element of group VI of the periodic table of the elements, and water, and recovering a 1,5-diol from the mixture.

5. A method of preparing 1,5-pentanediol comprising subjecting 2-(3,4-dihydro-1,2-pyran-1-yl) methyl ether to the simultaneous action of an aqueous acidic hydrolytic medium containing at least its molecular equivalent of water, and of hydrogen under a pressure from about 250 to about 10,000 pounds per square inch, in the presence of a hydrogenation catalyst and at a temperature from about 50° C. to about 350° C., and recovering 1,5-pentanediol from the resultant mixture.

6. A method of preparing 1,5-pentanediol comprising subjecting a 2-(3,4-dihydro-1,2-pyran-1-yl) organic ether wherein the 2-dihydropyran-1-yl group is unsubstituted, to the simultaneous action of an aqueous hydrolytic medium and hydrogen under a pressure from about 250 to about 10,000 pounds per square inch in the presence of hydrogenation catalyst at a temperature from about 50° C. to about 350° C. and recovering 1,5-pentanediol from the resultant mixture.

7. A method of preparing a 1,5-diol comprising subjecting in the presence of a hydrogenation catalyst a 3,4-dihydro-1,2-pyran having an organic substituent group attached to the carbon atom in position No. 2 of the dihydropyran ring by a hydrolyzable bond to a divalent atom of a non-metallic element of group VI of the periodic table of the elements, to the simultaneous action of an aqueous hydrolytic medium and hydrogen under conditions of an elevated temperature and a superatmospheric pressure of hydrogen conducive to hydrogenation reaction, and recovering a 1,5-diol from the resultant mixture.

8. The method of producing 1,5-pentanediol consisting in subjecting to simultaneous hydrolysis and hydrogenation in the presence of a hydrogenation catalyst an unsubstituted 2-(3,4-dihydro-1,2-pyranyl) lower alkyl ether.

9. The method of producing 1,5-pentanediol consisting in subjecting to simultaneous hydrolysis and hydrogenation in the presence of a hydrogenation catalyst an otherwise unsubstituted derivative of 3,4-dihydro-1,2-pyran having an organic substituent group attached to the carbon atom in position No. 2 of the dihydropyran ring by a hydrolyzable bond to a divalent atom of a non-metallic element of group VI of the periodic table of the elements.

10. The method of producing a 1,5-diol consisting in subjecting to simultaneous hydrolysis and hydrogenation in the presence of a hydrogenation catalyst a 3,4-dihydro-1,2-pyran having an organic substituent group attached to the carbon atom in position No. 2 of the dihydropyran ring by a hydrolyzable bond to a divalent atom of a non-metallic element of group VI of the periodic table of the elements.

11. The method of producing 1,5-pentanediol

from acrolein comprising the steps of condensing acrolein with a lower alkyl ether of vinyl alcohol by heating in admixture to produce a 2-(3,4-dihydro-1,2-pyranyl) lower alkyl ether, hydrogenating the products of the condensation reaction containing the 2-(3,4-dihydro-1,2-pyranyl) lower alkyl ether by treatment with hydrogen gas in the presence of water and a hydrogenation catalyst, and recovering 1,5-pentanediol from the products of the hydrogenation.

12. The method of producing a 1,5-diol from an alpha,beta-olefinic aldehyde which comprises condensing the alpha,beta-olefinic aldehyde with a vinyl compound of the general formula



wherein R denotes a hydrocarbon group to produce a 2-(3,4-dihydro-1,2-pyranyl) ether having the group denoted by R linked to the ether oxygen atom, and subjecting said ether to the action of molecular hydrogen in the presence of a hydrogenation catalyst and water at an elevated temperature and under a superatmospheric pressure of hydrogen gas to produce a 1,5-diol.

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