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PROCESS FOR PRODUCING SATURATED DIOLS
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ABSTRACT OF THE DISCLOSURE

Process for producing a saturated 1,4-diol which comprises hydrogenating the corresponding acetylenic 1,4-diol at a temperature of 15°–125° C. and a pressure of 15–500 p.s.i.g. in the presence of a platinum, palladium or rhodium catalyst and a solvent selected from the group consisting of benzene, ethylbenzene, p-isopropyltoluene, dibutyl carbitol and mixtures thereof.

This invention relates to a process for preparing saturated diols. More particularly, this invention relates to a process for producing saturated 1,4-diols which involves catalytically hydrogenating the corresponding acetylenic 1,4-diol in the presence of certain solvents.

The preparation of saturated 1,4-diols by catalytically hydrogenating the corresponding acetylenic 1,4-diol is well known and has heretofore been effected by processes which vary primarily in the utilization of different catalyst systems. Many of these prior processes, however, were not satisfactory either in achieving complete saturation of the acetylenic bond or in producing the completely saturated diol at the level of yield and in the degree of purity required for successful commercial operation. For example, in a process utilizing a nickel-alkaline or Raney nickel catalyst, hydrogenation of an acetylenic diol effected the reduction of only one of the triple bonds with the result that olefinic or only partially saturated diols were the principal product of the hydrogenation. Other processes, however, using different catalysts, such as platinum or palladium, did effect the complete saturation of the acetylenic bond, but concomitantly with the production of the desired fully saturated diol product there were also produced substantial quantities of hydrogenolysis side products such as saturated mono-alcohols and saturated hydrocarbons which resulted in the yield being reduced to a very low level of the order of only about 10 to 32 percent.

Recently, a process was developed which permitted the use of catalysts such as platinum and palladium to effect the complete saturation of the acetylenic bond, but which also avoided the simultaneous production of substantial quantities of the yield-reducing hydrogenolysis products. This highly desirable result was achieved in this process by utilizing a small quantity of alkaline material such as potassium or sodium hydroxide in conjunction with the catalyst to substantially suppress the formation of the undesirable hydrogenolysis products. It has now been discovered, however, that the hydrogenation can also be effected with such catalysts as platinum and palladium without the use of alkaline materials and moreover in remarkably high yields and purity and with low hydrogenolysis side product formation by conducting the hydrogenation in the presence of certain solvents.

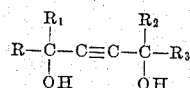
Accordingly, it is an object of this invention to provide a process for producing saturated 1,4-diols in high yield and high purity. Another object is to provide a process for producing saturated 1,4-diols by catalytically hydrogenating the corresponding acetylenic 1,4-diol which avoids substantially hydrogenolysis product formation. Still another object of this invention is to provide a process for effecting the hydrogenation in a simple and

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economical manner which does not require the use of alkaline materials to suppress or prevent hydrogenolysis side reactions.

The above objectives are achieved according to this invention by conducting the complete hydrogenation of acetylenic 1,4-diols to the corresponding saturated 1,4-diol in the presence of a catalyst selected from the group consisting of platinum, palladium and rhodium and a solvent selected from a group consisting of benzene, ethylbenzene, p-isopropyltoluene and dibutyl carbitol. By conducting the hydrogenation in the presence of such solvents, it has been discovered that the alkaline materials heretofore believed to be essential in preventing hydrogenolysis are not required. Moreover, the use of such solvents according to this invention in conjunction with the catalysts has resulted in the obtaining of extremely high yields of highly pure saturated 1,4-diols. Not only, however, has the use of these particular solvents resulted in both an improved and greatly simplified process by avoiding the required use of alkaline materials, but other notable and valuable advantages have also resulted therefrom, one of the principal ones being the highly desirable processing feature of greatly extended catalyst life which permits extensive catalyst reuse without costly reactivation or replacement. Still another advantage, which results from the substantial insolubility of the saturated diol in the particular solvents of this invention at relatively low temperatures, is that separation of the product in highly pure form is readily and easily effected by simply cooling the liquid hydrogenation reaction mixture and filtering the solid precipitate which forms.

The acetylenic 1,4-diols which may be effectively hydrogenated to the corresponding fully saturated 1,4-diol according to the process of this invention have the following general structure:



wherein R, R₁, R₂ and R₃ designate respectively hydrogen, or the same or different alkyl, cycloalkyl, or aryl groups. Examples of these acetylenic 1,4-diols include: 2,5-dimethyl-3-hexyne-2,5-diol, 3,6-dimethyl-4-octyne-3,6-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 4,7-dimethyl-5-decyne-4,7-diol, 2,5-diphenyl-3-hexyne-2,5-diol, 2,5-dicyclohexyl-3-hexyne-2,5-diol or 4-ethyl-7-methyl-5-nonyne-4,7-diol.

The solvents hereinbefore referred to and comprising the group of benzene, ethylbenzene, p-isopropyltoluene, and dibutyl carbitol, also defined as the dibutyl ether of diethylene glycol, which are used in the hydrogenation of this invention to substantially suppress formation of hydrogenolysis side reactions and thereby avoid the necessity of using alkaline materials generally different in their effect upon the hydrogenation. Of the different solvents within the group, the most desirable results in respect to lower hydrogenolysis side product formation and desirable product yield and purity have been obtained with ethylbenzene and accordingly it is the preferred solvent for the hydrogenation. The solvents within this group may be used separately or in admixtures and even may be used with small proportions of other suitable solvents such as alkyl substituted benzenes or alkanes. The quantity of solvents used in the hydrogenation is not critical and may be widely varied with a solvent weight ranging from about one half to two times the weight of the 1,4-diol being satisfactory for most hydrogenations. Generally, optimum results are achieved when the solvent is used in an amount substantially equal in weight to the weight of the acetylenic 1,4-diol being hydrogenated.

As hereinbefore indicated, the hydrogenation catalyst

utilized in conjunction with the particular solvents of this invention is selected from the group consisting of platinum, palladium and rhodium. The activities of the catalysts vary in respect to achieving complete saturation of the acetylenic bond and in simultaneously promoting hydrogenolysis side reactions. Of the catalysts within this group, the most desirable results have been obtained with palladium and accordingly it is the preferred catalyst for the hydrogenation according to this invention. The quantity of metal catalyst used in the hydrogenation is not critical and may be used in any amount normally used for hydrogenation reactions. This amount may range from about 0.01 to 2.0 weight percent of metal catalyst based upon a total weight of the solvent and acetylenic diol with a preferred amount being within the range of from about 0.02 to 0.15 weight percent. Consistent with normal hydrogenation practice, the metal catalyst is preferably supported on an inert carrier such as for example a neutral clay or charcoal. When a carrier is utilized, the preferred carrier is charcoal and a highly usable catalyst for the hydrogenation according to this invention is a palladium charcoal catalyst which contains about 5 percent by weight of palladium.

The hydrogenation process of this invention which is effected in the presence of the particular aforementioned solvents is conducted under relatively moderate temperatures and pressures. Generally, the temperature may range from about 15° to about 125° C. and preferably from 25° to about 95° C., with the pressure generally ranging from about 15 to 500 pounds per square inch gage and preferably from about 15 to 105 pounds per square inch gage. If the hydrogenation is conducted at too low a temperature the time required for complete saturation is generally too long for commercial operation and if the hydrogenation is conducted at too high a temperature the production of the undesired hydrogenolysis products is favored. Inasmuch as the first phase of the reaction, namely the partial saturation of the acetylenic bond to a double bond is exothermic, no heating is generally required with small scale hydrogenation equipment and only slight cooling with larger equipment to maintain the temperature in the desired operating range. However, after the first phase of the reaction is completed, external heating is generally required to maintain the reaction. The time required for the hydrogenation will vary depending upon such factors such as reaction temperature, the particular solvent used, and the type and quantity of catalyst. Generally, the hydrogenation is carried out until there is a cessation of hydrogen absorption as measured by no further drop in the hydrogen pressure which indicates complete saturation of the acetylenic bond.

The hydrogenation process of this invention may be conducted in a batch, semi-continuous or continuous type of operation. For example, a batch-type of operation may be illustrated as follows: an acetylenic 1,4-diol, for example 2,5-dimethyl-3-hexyne-2,5-diol, together with about

bination of both. After completion of the first phase of the reaction wherein the acetylenic bond is partially saturated as signified by adsorption of about one-half the hydrogen theoretically required, external heat is supplied to maintain the desired temperature and sustain the reaction. When the hydrogen pressure has dropped to the level indicating absorption of the amount of hydrogen theoretically required to completely saturate the acetylenic bond, the temperature is raised to a substantially higher temperature for a short period to insure complete reaction. While the vessel is still hot the contents are removed and filtered to separate the catalyst which because of the unique action of the solvent according to this invention may be reused without reactivation or replacement for another hydrogenation. The recovered liquids are then treated by conventional methods to separate the saturated diol from the solvent. For example, the liquid reaction mixture is cooled to about 25° C. and the solid product which precipitates is separated by filtration from the liquid solvent and dried to recover the highly pure diol product which in this illustration will be 2,5-dimethyl-hexane-2,5-diol.

The following examples are given to illustrate the hydrogenation process of this invention which are not, however, intended to limit the generally broad scope of this invention in strict accordance therewith:

Example I

A series of hydrogenations were conducted in which the catalyst was reused for the succeeding hydrogenations according to the following general procedure:

About 453 grams of 2,5-dimethyl-3-hexyne-2,5-diol and about 453 grams of ethylbenzene were charged to a mild steel Aminco rocking autoclave containing about 9.0 grams of palladium charcoal catalyst (5% by weight palladium). After purging with hydrogen the autoclave pressure was raised with hydrogen to about 100 pounds per square inch gage. The reaction proceeded exothermically raising the temperature to about 58° to 60° C. with the pressure dropping to the level indicating adsorption of about one half the hydrogen theoretically required. As the reaction mixture began to cool, external heat was supplied to maintain the temperature within the range of about 65° to 80° C. When the pressure had dropped to the level indicating adsorption of the quantity of hydrogen theoretically required for complete saturation, the temperature was then raised to about 90° C. for a brief period to insure complete reaction. While the autoclave was still hot the reaction mixture was removed and filtered to recover the catalyst which was returned to the autoclave for the next hydrogenation. The liquid reaction mixture was then cooled to about 25° C. and filtered to recover the solids which precipitated from the ethylbenzene solvent. The solids were washed with heptane at about 0° C., and dried to recover the desired 2,5-dimethylhexane-2,5-diol product. The conditions and results of the hydrogenations are summarized in Table I.

TABLE I

Hydrogenation	I	II	III	IV	V	VI
Temperature Range, ° C.	25-90	25-90	25-90	25-90	25-90	25-90
Reaction Time, Hours	1.0	4.0	3.5	1.5	1.75	2.0
Weight Crude Product, Grams	759	870	893	894	865	833
Hydrogenolysis Products, percent by Weight	0	3.4	2.1	2.9	0.2	0.6
Yield, percent	87.0	87.8	84.3	88.4	86.2	88.9
Purity, percent	100	93.4	95.4	94.1	99.5	99.0

Example II

an equal weight of solvent such as the preferred ethylbenzene is charged to a suitable hydrogenation vessel containing the catalyst such as the preferred palladium charcoal. Hydrogen is then charged to the vessel to the desired pressure. The reaction proceeds with the temperature rising to the desired range due either to the exothermic heat generated or by external heating or a com-

A series of hydrogenations were conducted in a Parr hydrogenation bottle at pressures ranging from about 50 to 20 pounds per square inch gage according to the general procedure outlined in Example I. In this series of hydrogenations, as in Example I, the fresh catalyst used in the first hydrogenation was reused for the succeeding

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hydrogenations. The weights of the acetylenic diol, solvent and catalyst used for the hydrogenations were as follows:

2,5-dimethyl-3-hexyne-2,5-diol	G.
Ethylbenzene	71
Palladium charcoal catalyst (5% palladium)	1.4

The conditions and results of the hydrogenations are summarized in Table II.

TABLE II

Hydrogenation	VII	VIII	IX	X
Temperature, Range, ° C.	21-52	18-25	20-95	18-95
Reaction Time, Hours	2.75	1.0	1.5	4.0
Hydrogen Adsorbed, Percent Theory	109.05	110	110	110
Weight, Crude Product, Grams	137.0	140.1	136.3	134.0
Hydrogenolysis Products, Percent by Weight	0.18	0.69	1.6	1.91
Yield, Percent	80.05	98.0	86.0	82.2

Example III

A series of hydrogenations were conducted in a Parr hydrogenation bottle at pressure ranging from about 50 to 20 pounds per square inch gage in the presence of different solvents according to the general procedure outlined in Example I. The conditions and results of the hydrogenations are summarized in Table III.

TABLE III

Hydrogenation	XI	XII	XIII
Solvent	Benzene	p-Iso-propyl toluene	Dibutyl-Carbitol
Weight of Solvent, Grams	71	71	142
Weight 2,5-dimethyl-3-hexyne-2,5-diol, Grams	71	71	142
Weight 5% Palladium Charcoal Catalyst, Grams	1.4	1.4	2.0
Temperature Range, ° C.	25-93	25-84	25-85
Time, Hours	1	1.75	9
Hydrogen Adsorbed, Percent Theory	110	114	109
Weight of Crude Product, Grams		132	
Hydrogenolysis Product, Percent by Weight	2.0	2.25	0
Yield, Percent			90
Melting Point, ° C.			87-88

Example IV

The hydrogenation process of this invention is conducted with a platinum catalyst according to the following procedure:

About 453 grams of 3,6-dimethyl-4-octyne-3,6-diol and about 453 grams of ethylbenzene are charged to a mild steel Aminco rocking autoclave containing about 9.0 grams of platinum charcoal catalyst (5% platinum). After purging with hydrogen the autoclave pressure is raised with hydrogen to about 100 pounds per square inch gage. The reaction proceeds exothermically raising the temperature to about 58 to 60° C. As the reaction mixture begins to cool, external heat is supplied to maintain the temperature at about 65° to 80° C. When the pressure drops to the level indicating adsorption of the quantity of hydrogen theoretically required for complete saturation, the temperature is raised to about 90° C. for a brief period to insure complete reaction. While the autoclave is still hot the reaction mixture is removed and filtered to separate the catalyst. The liquid reaction mixture is then cooled to about 25° C. and filtered to separate the solids which precipitate from the solvent. The recovered solids are then dried to recover the desired 3,6-dimethyloctane-3,6-diol in high yield and purity.

Example V

The hydrogenation process of this invention is conducted with a rhodium catalyst according to the following procedure:

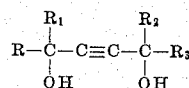
About 453 grams of 4,7-dimethyl-5-decyne-4,7-diol and about 453 grams of ethylbenzene are charged to a mild steel Aminco rocking autoclave containing about 9.0 grams of rhodium charcoal catalyst (5% rhodium). After purging with hydrogen the autoclave pressure is raised

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with hydrogen to about 100 pounds per square inch gage. The reaction proceeds exothermically raising the temperature to about 58 to 60° C. As the reaction mixture begins to cool, external heat is supplied to maintain the temperature at about 65° to 80° C. When the pressure drops to the level indicating adsorption of the quantity of hydrogen theoretically required for complete saturation, the temperature is raised to about 90° C. for a brief period to insure complete reaction. While the autoclave is still hot the reaction mixture is removed and filtered to separate the catalyst. The liquid reaction mixture is then cooled to about 25° C. and filtered to separate the solids which precipitate from the solvent. The recovered solids are then dried to recover the desired 4,7-dimethyldecane-4,7-diol in high yield and purity.

We claim as our invention:

1. A process for producing a saturated 1,4-diol which comprises hydrogenating an acetylenic 1,4-diol having the formula



wherein R, R₁, R₂ and R₃ are independently selected from the group consisting of hydrogen, lower alkyl, cyclohexyl and phenyl, at a temperature of from about 15° to 125° C. and a pressure of from about 15 to 500 pounds per square inch gage in the presence of a hydrogenation catalyst system consisting of a catalyst selected from the group consisting of platinum, palladium and rhodium and a solvent selected from the group consisting of benzene, ethylbenzene, p-isopropyltoluene, dibutyl carbitol and mixtures thereof, the weight ratio of solvent to acetylenic diol being in the range of from about 1:2 to 2:1, and recovering as the desired product the corresponding saturated 1,4-diol.

2. The process of claim 1 further characterized in that the hydrogenation is effected at a temperature of from about 25° to 95° C. and a pressure of from about 15 to 105 pounds per square inch gage.

3. A process for producing 2,5-dimethylhexane-2,5-diol which comprises hydrogenating 2,5-dimethyl-3-hexyne-2,5-diol feed at a temperature in the range of from about 25° to 95° C. and a pressure of from about 15 to 105 pounds per square inch gage in the presence of a catalyst system consisting of a palladium catalyst and an ethylbenzene solvent, the weight ratio of solvent to feed being in the range of from about 1:2 to 2:1, and recovering the desired product.

4. A process for producing 2,5-dimethylhexane-2,5-diol which comprises hydrogenating 2,5-dimethyl-3-hexyne-2,5-diol feed at a temperature in the range of from about 25° to 95° C. and a pressure of from about 15 to 105 pounds per square inch gage in the presence of a catalyst system consisting of a palladium catalyst and a p-isopropyltoluene solvent, the weight ratio of solvent to feed being in the range of from about 1:2 to 2:1, and recovering the desired product.

5. A process for producing 2,5-dimethylhexane-2,5-diol which comprises hydrogenating 2,5-dimethyl-3-hexyne-2,5-diol feed at a temperature in the range of from about 25° to 95° C. and a pressure of from about 15 to 105 pounds per square inch gage in the presence of a catalyst system consisting of a palladium catalyst and a benzene solvent, the weight ratio of solvent to feed being in the range of from about 1:2 to 2:1, and recovering the desired product.

6. A process for producing 2,5-dimethylhexane-2,5-diol which comprises hydrogenating 2,5-dimethyl-3-hexyne-2,5-diol feed at a temperature in the range of from about 25° to 95° C. and a pressure of from about 15 to 105 pounds per square inch gage in the presence of a catalyst system consisting of a palladium catalyst and a dibutyl carbitol solvent, the weight ratio of solvent to feed being in the

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range of from about 1:2 to 2:1, and recovering the desired product.

7. A process for producing 3,6-dimethyloctane-3,6-diol which comprises hydrogenating 3,6-dimethyl-4-octyne-3,6-diol feed at a temperature in the range of from about 25° to 95° C. and a pressure of from about 15 to 105 pounds per square inch gage in the presence of a catalyst system consisting of a platinum catalyst and an ethylbenzene solvent, the weight ratio of solvent to feed being in the range of from about 1:2 to 2:1, and recovering the desired product.

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