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PRODUCTION OF CYCLODODECANOL

Friedrich Urbanek, Schifferstadt (Pfalz), Germany, assignor to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

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This invention relates to the production of cyclododecanol from cyclododecatriene.

It is known that by the action of organic peracids or other organic per compounds on cyclododecatriene-(1,5,9) it is possible to obtain 1,2-epoxycyclododecadiene-(5,9) which can be hydrogenated to cyclododecanol. Although the hydrogenation in general offers no particular difficulty, the use and handling of organic peracids constitutes an obstacle to carrying out the reaction on a large scale.

It is an object of this invention to provide a process by which cyclododecanol can be prepared in a simple way from cyclododecatriene on a large scale. It is another object of the invention to provide a process for the production of 1,2-epoxycyclododecadiene and of cyclododecanol in which the use of peracids is avoided. It is a further object of the invention to provide a process in which cyclododecanol is obtained in higher yields than hitherto from cyclododecatriene. These and other objects and advantages of the invention will become apparent from the following detailed description.

I have found that cyclododecanol is obtained from cyclododecatriene-(1,5,9) by bringing the latter, if desired dissolved in a solvent, into contact with oxygen or a gas containing oxygen at a temperature of 20° to 200° C. in the presence of heavy metal oxidation catalysts while agitating the mixture, distilling the reaction product thus obtained and then hydrogenating the fraction substantially consisting of cyclododecadiene epoxide by a conventional method to cyclododecanol.

The initial material is cyclododecatriene-(1,5,9) and it is not important whether one or other geometrical isomer is used. Both the trans-trans-cis-compound and the trans-trans-trans-compound may be used.

Pure oxygen may be used but it is preferred to carry out the oxidation with air or with a mixture of oxygen and inert gas in which the proportion of oxygen is about 3 to 30 volume percent. Apart from nitrogen, the chief inert gas is carbon dioxide.

It is preferred to carry out the reaction at 100° to 150° C. within the said temperature range.

The process is usually carried out under atmospheric pressure, it may however also be carried out at superatmospheric pressure, for example at 2 to 20 atmospheres or at higher pressures.

Carrying out the process at superatmospheric pressure is particularly important when the solvent used is relatively volatile. Examples of solvents are low molecular weight alkanecarboxylic acids, especially those having two to five carbon atoms, or benzene.

The oxidation catalysts may be compounds and salts of heavy metals conventionally used in oxidation processes, such as silver, copper, vanadium, molybdenum, chromium, tungsten, manganese, iron, nickel and especially cobalt, and also the metals of the platinum group. Oxides, chlorides, bromides or phthalocyanines may be used but it is preferred to use the salts of organic acids, particularly those whose salts dissolve in cyclododecatriene, such as naphthenates, stearates or in general salts of higher alkane monocarboxylic and dicarboxylic acids having six to twenty-five carbon atoms. The following

are given as examples of suitable oxidation catalysts: cobalt naphthenate, cobalt ethylhexanate, silver stearate, cobalt bromide, copper phthalocyanine and manganese stearate. The various oxidation catalysts are generally used in amounts of 0.001 to 1% by weight with reference to cyclododecatriene. Oxidation may however also be carried out at higher catalyst concentrations.

When using soluble metal catalysts, the process is carried out in homogeneous liquid phase. When using insoluble catalysts, for example oxides or chlorides of heavy metals, the catalyst may also be rigidly arranged, for example on carriers, and the reactants passed over the catalyst in cocurrent or countercurrent. Examples of carriers for the supported catalysts are: silica gel, pumice, aluminum oxide, active carbon or magnesium silicate.

The catalytic activity of the oxidation catalysts can be improved by adding nitrogen bases in amounts of 0.001 to 1.0% by weight, with reference to cyclododecatriene. Suitable nitrogen bases are quaternary ammonium bases having as substituents one to four alkyl radicals of which any two may be combined together with the inclusion of the nitrogen to form a ring, the total number of carbon atoms in the bases being from one to sixteen.

The oxidation of cyclododecatriene may also be carried out with the addition of a solvent, for example a lower alkanecarboxylic acid, such as acetic acid, propionic acid, butyric acid, or an anhydride of such an acid. It is however also possible to use benzene or chlorobenzene, for example, as the solvent. The solutions should initially contain at least 20% of cyclododecatriene so that the process may be economical.

In general the process of catalytic oxidation of cyclododecatriene is carried out with conversions of only 2 to 20%, but preferably 3 to 10%. In this way yields of cyclododecadiene epoxide of about 50 to 65% with reference to reacted cyclododecatriene are achieved.

After oxidation, the reaction mixture, advantageously with an addition of conventional polymerization inhibitors, such as thiodiphenylamine, in amounts of 0.001 to 0.01% by weight, is distilled at atmospheric pressure or subatmospheric pressure. A fraction is thus obtained consisting of unreacted cyclododecatriene, another fraction containing solvent (when such has been used) and a fraction consisting substantially of cyclododecadiene epoxide.

The cyclododecadiene epoxide fraction has a boiling point dependent on the pressure used for the distillation, for example in the range of 85° to 110° C. at 0.5 mm. Hg pressure. Cyclododecadiene epoxide may also be isolated by fine distillation in pure form (boiling point 100° C. at 0.5 mm. Hg) and then hydrogenated.

It has proved to be advantageous however not to isolate the cyclododecadiene epoxide in pure form but to use the relatively wide fraction which passes over in a simple distillation as cyclododecadiene epoxide but which also contains a number of other oxidation products (not determined more exactly) and to subject it direct to hydrogenation under conventional conditions, for example at temperatures of 100° to 140° C. and pressures of 100 to 200 atmospheres using prior art hydrogenation catalysts, for example Raney nickel, Raney cobalt, copper catalysts or supported catalysts, for example nickel on silica gel. The catalysts are used in amounts of 1 to 10% by weight with reference to the amount supplied to the hydrogenation.

The process may therefore be carried out for example as follows:

One of the abovementioned oxidation catalysts is added to cyclododecatriene (used either in pure state or as an at least 20% solution) and then oxygen or air is passed therethrough. Supply of oxygen is discontinued as soon as 5 to 10% of the cyclododecatriene has been ox-

idized. The period required for the oxidation is advantageously determined by laboratory experiment and analytical processing after different periods, the period then being applicable always for the particular conditions used.

The reaction mixture obtained is then distilled, preferably under reduced pressure. A relatively wide fraction separates for cyclododecadiene epoxide. This fraction is then contacted with hydrogen using a hydrogenation catalyst, either by passing hydrogen through the said fraction or by allowing the fraction to trickle over a rigidly arranged catalyst and passing hydrogen cocurrent or countercurrent. The catalyst is then separated and further worked up by distillation, preferably under subatmospheric pressure.

The following examples will further illustrate the invention.

Example 1

A current of air at the rate of 35 liters per hour is passed for half an hour at 130° C. through 500 g. of cyclododecatriene-(1,5,9) in which 0.05 g. of silver stearate has been dissolved, in an electrically heated glass tube having a diameter of 35 mm. and a length of 700 mm. The reaction mixture is then distilled at a pressure of 0.5 mm. Hg. 456 g. of unreacted cyclododecatriene is obtained and at 100° to 120° C. a fraction consisting mainly of cyclododecadiene epoxide.

This fraction is dissolved in 80 ml. of ethanol and hydrogenated under a hydrogen pressure of 200 atmospheres gauge in an autoclave at 120° C. in the presence of 5 g. of Raney nickel. 25 g. of cyclododecanol (50.1% of the theory with reference to cyclododecatriene) is obtained from the hydrogenation mixture by distillation.

Example 2

A finely dispersed stream of air at 130° C. is passed for half an hour at the rate of 30 liters per hour through 1500 g. of cyclododecatriene-(1,5,9) in which 0.05 g. of cobalt ethylhexanate has been dissolved and which is contained in a two-liter three-necked flask provided with stirring means and a reflux condenser, with continuous agitation. The reaction mixture obtained is distilled. 25 g. of a fraction consisting substantially of cyclododecadiene epoxide is obtained at 85° to 110° C. and 0.3 mm. Hg. This is then hydrogenated as in Example 1. 23 g. of cyclododecanol is obtained. The yield, with reference to reacted cyclododecatriene, is 62% of the theory.

I claim:

1. Process for the production of cyclododecanol from cyclododecatriene-(1,5,9) which comprises passing a gas selected from the group consisting of oxygen and gases containing oxygen in free molecular form through cyclododecatriene-(1,5,9) at a temperature of from 20° to 200° C. at a pressure of from 2 to 20 atmospheres in the presence of an oxidation catalyst for a period of time sufficient to produce a conversion of from about 2 to about 20%, distilling the reaction mixture obtained, separating a fraction containing substantial amounts of cyclododecadiene epoxide and contacting said cyclododecadiene epoxide fraction with hydrogen at a temperature of from 100° to 140° C. at a pressure of 100 to 400 atmospheres in the presence of a hydrogenation catalyst.

2. A process as claimed in claim **1**, in which the oxidation catalyst used is a cobalt compound.

3. A process as claimed in claim **1**, in which the hydrogenation catalyst is Raney nickel.

4. A process as in claim **1** wherein the oxidation is carried out for a sufficient period of time to produce a conversion of from 3 up to 10%.

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LEON ZITVER, *Primary Examiner.*

T. G. DILLAHUNTY, *Assistant Examiner.*