

PATENT SPECIFICATION

(11) 1 580 665

1 580 665

(21) Application No. 32888/77 (22) Filed 5 Aug. 1977

(31) Convention Application No. 2635396

(32) Filed 6 Aug. 1976 in

(33) Federal Republic of Germany (DE)

(44) Complete Specification published 3 Dec. 1980

(51) INT CL³ C07C 31/18

(52) Index at acceptance

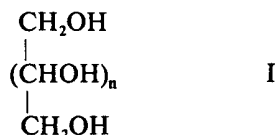
C2C 20Y 30Y 360 361 362 36Y 383 502 50Y 643 66Y FB YP



(54) MANUFACTURE OF SUGAR ALCOHOLS

(71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to an improved process for the manufacture of sugar alcohols of the general formula I



where

n is from 2 to 5.

Sugar alcohols may be manufactured by reducing the corresponding aldoses (J. Stanek et al "The Monosaccharides", Academic Press, London, 1963, page 626), but at the same time sugar acids, or the lactones of these acids, form easily (Chemikerzeitung, 99 (1975), 450), and furthermore some aldoses are only obtainable with difficulty.

The sugar alcohols I can further be manufactured by catalytically hydrogenating aldonic acid lactones over platinum oxide catalysts (J. Am. Chem. Soc., 57 (1935), 2,204 et seq.), but both because of the expensive catalyst and because of the unsatisfactory yields, this method is unsuitable for industrial syntheses. Finally, D-gluconic acid lactone has been hydrogenated by means of catalysts containing copper oxide and chromium oxide at 250°C; however, this did not give any sorbitol, but only propanediol and ethylene glycol as scission products.

Since the sugar alcohols I are of great importance, inter alia as a sugar substitute for diabetics, as intermediates for vitamins (sorbitol, for example, being an intermediate for vitamin C) and for other

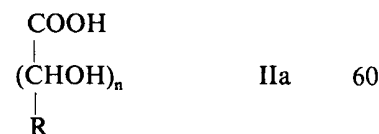
physiologically active compounds and also, for example in the manufacture of alkyl resins and explosives, the present invention seeks to provide a technically and economically improved method of obtaining these compounds.

According to the invention there is provided an improved process for the manufacture of a sugar alcohol of the general formula I



where

n is from 2 to 5, by hydrogenating a p- or δ-lactone (II) which is derived from an aldonic acid of the general formula IIa



where

n has the above meaning and

R is —CH₂OH or —COOH, by means of hydrogen over a catalyst containing copper oxide, in which process the catalyst used is a mixed oxide comprising from 20 to 95% by weight of copper oxide (calculated as CuO) and from 5 to 80% by weight of chromium oxide (calculated as Cr₂O₃) and/or aluminum oxide, and the hydrogenation is carried out at from 70 to 200°C.

Cu-Cr mixed oxides which can be used as catalysts according to one embodiment of the invention are disclosed in Organic Reactions, 8 (1954), 8 et seq. As stated there, the mixed oxides are neither a mechanical mixture of Cu oxide and Cr oxide nor copper chromite, but compounds intermediate between these two extreme states. Since the material is presumably a mixture of the oxides at the atomic level, so

that an interaction between the Cu atoms and Cr atoms can occur, the mixed oxides are best manufactured by coprecipitation from an aqueous solution, containing a Cu salt and a chromate, by means of a base, e.g. ammonia. Further details may be found in the above publication and in the monograph by F. Zymalkowski, "Katalytische Hydrierung," (Enke-Verlag, Stuttgart), pages 32 et seq. In general terms, similar remarks apply to catalysts containing Cu and Al, and catalysts containing Cu, Cr and Al, which are used in other embodiments of the invention. In addition, it is at times advisable to use up to 10%, by weight, based on the weight of the mixed oxide as defined above, of a promoter, principally barium oxide.

The basic mixed oxides first obtained may be converted into the oxides by heating in air. Since these oxides only display their full catalytic activity after a certain start-up stage under hydrogenating conditions, it is advisable to pretreat them at from 150 to 250°C and from 0.01 to 100 bars partial pressure of hydrogen for at least 2 hours, preferably from 2 to 8 hours, before using them for their intended purpose. Catalysts pretreated in this way are then fully active from the start.

The active catalyst composition can also be applied to supports, e.g. silica gel, by conventional techniques.

Preferred catalysts are those where the atomic ratio of Cu to Cr and/or Al is of the order of 1:1, i.e. is from 1:0.7 to 1:1.5.

The amount of catalyst used is preferably from 1 to 100 g of active metal oxide per mole of the lactone II to be hydrogenated.

Within the stated temperature range of from 70 to 200°C, the range from 120 to 150°C is preferred. The hydrogen pressure is not critical and may vary within the wide limits of from 1 to 1,000 bars. As a rule, the optimum for technological purposes is from 100 to 300 bars.

Since heterogeneous catalysis is concerned it is advantageous, to achieve satisfactory space-time yields, if the starting compound II and product I are present in a homogeneous liquid phase. It is therefore in most cases advisable to use an inert solvent, e.g. water or dioxane. Lower alcohols, e.g. methanol, ethanol, propanols or butanols, may also be used. Suitable solvents, and their amounts, can easily be found by a few preliminary experiments.

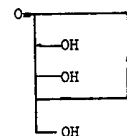
The starting compounds II are γ -lactones or δ -lactones (having the D-, L- or DL-configuration) of aldonic acids of 4 to 7 carbon atoms, e.g. gluconic acid, mannonic acid, gulonic acid, galactonic acid, allonic acid, altronic acid, heptonic acid, ribonic acid, arabonic acid, xylonic acid, lyxonic

acid, erythronic acid and threonic acid, especially D-gluconic acid γ -lactone, D-gluconic acid δ -lactone, D-mannonic acid γ -lactone, D-mannonic δ -lactone, D-ribonic acid γ -lactone and D-arabonic acid γ -lactone, as well as lactones of aldaric acids (sugar acids), e.g. D-saccharic acid, D-mannonic and mucic acid. The said lactones are known from the literature and some of them are commercially available, whilst many are more easily accessible than the corresponding aldoses, from which the sugar alcohols I have been manufactured hitherto. On the other hand, in the last-mentioned reaction the lactones II are formed as by-products which can then also be converted, by the process of the invention, into the desired compounds I.

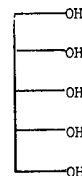
Generally, the corresponding sugar alcohols are obtained in yields of from 70 to 95%, the remainder consisting almost exclusively of the epimeric alcohols which form under the reaction conditions. If the pure products are required, the materials obtained may be worked up by recrystallization in the conventional manner.

EXAMPLE 1

29.6 (0.2 mole) of D-ribonic acid γ -lactone



in 150 ml of dioxane were hydrogenated in the course of 48 hours at 120°C and 170 bars hydrogen pressure by means of 6 g of a mixed oxide catalyst comprising 45% by weight of copper oxide (calculated as CuO) and 55% by weight of chromium-III oxide. After concentrating the catalyst-free solution, removing the crystals formed and recrystallizing the product from 250 ml of ethanol, the final product, ribitol

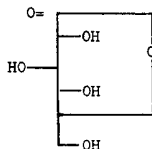


was obtained in 89% yield. The remainder consisted of isomeric sugar alcohols of 5 carbon atoms.

The catalyst was manufactured by first precipitating basic oxides from aqueous Cu nitrate/Na chromate solutions by means of ammonia, and then converting these basic oxides to the oxides by heating in air.

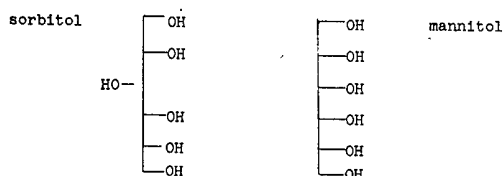
EXAMPLE 2

74.2 g (0.4 mole) of D-gluconic acid δ -lactone



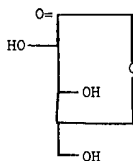
- 5 where hydrogenated in 150 ml of dioxane at 135°C and 250 bars hydrogen pressure in the course of 48 hours over 18 g of a catalyst comprising 52% by weight of copper oxide (calculated as CuO) and 48% by weight of aluminum oxide, the catalyst having been pretreated under hydrogenating conditions (200 bars of H₂; 200°C; 8 hours). Working up in the conventional manner gave 70% of sorbitol and 15% of manitol.

The catalyst was manufactured from Cu nitrate and Na aluminate by a method analogous to that described in Example 1



20 EXAMPLE 3

38 g (0.257 mole) of D-arabonic acid γ -lactone



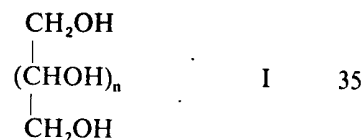
- 25 in 250 ml of dioxane were hydrogenated at 120°C and 170 bars hydrogen pressure, using 10 g of the catalyst described in Example 2. The residue obtained after removing the catalyst and the solvent consisted mainly of D-arabitol



and some ribitol.

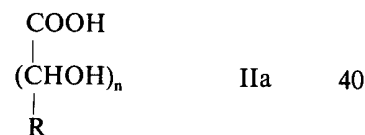
WHAT WE CLAIM IS:—

1. A process for the manufacture of a sugar alcohol of the general formula I



where

n is from 2 to 5, by hydrogenating a γ - or δ -lactone (II) which is derived from an aldonic acid of the general formula IIa



where

n has the above meaning and R is —CH₂OH or —COOH and n has the meaning given above, by means of hydrogen over a catalyst containing copper oxide, wherein the catalyst used is a mixed oxide comprising from 20 to 95% by weight of copper oxide (calculated as CuO) and from 5 to 80% by weight of chromium oxide (calculated as Cr₂O₃) and/or aluminum oxide, and the hydrogenation is carried out at from 70 to 200°C.

2. A process as claimed in claim 1, wherein the mixed oxide has been manufactured by coprecipitation from an aqueous solution containing a copper salt and a chromate and/or an aluminate by means of a base, followed by heating in air to convert the basic mixed oxides obtained in the coprecipitation into oxides.

3. A process as claimed in claim 1 or 2, wherein the mixed oxide catalyst has been pretreated at from 150 to 250°C and from 0.01 to 100 bars partial pressure of hydrogen for at least 2 hours prior to use in the hydrogenation reaction.

4. A process as claimed in any of claims 1 to 3, wherein the catalyst contains up to 10% by weight, based on the mixed oxide, of barium oxide as promoter.

5. A process as claimed in any of claims 1 to 4, wherein the atomic ratio Cu:Cr and/or Al in the mixed oxide is from 1:0.7 to 1:1.5.

6. A process as claimed in any of claims 1 to 5, wherein from 1 to 100 g of metal oxide is employed per mole of γ - or δ -lactone to be converted.

7. A process as claimed in any of claims 1 to 6, wherein the hydrogenation is carried out at from 120 to 150°C.

8. A process as claimed in any of claims 1 to 7, wherein the hydrogen pressure is from 100 to 300 bars.

9. A process as claimed in any of claims 1 to 8, wherein the hydrogenation is carried out with the starting lactone and product in a homogeneous liquid phase in an inert solvent.

10. A process as claimed in any of claims 1 to 9, wherein the lactone is the γ - or δ -lactone of D-gluconic acid or D-mannonic acid or is D-ribonic acid γ -lactone or D-arabonic acid γ -lactone.
11. A process for the manufacture of a sugar alcohol carried out substantially as described in any of the foregoing Examples.
12. Sugar alcohols when manufactured by a process as claimed in any of claims 1 to 11.
13. Vitamins and other physiologically active compounds, and alkyd resins and explosives, when made from sugar alcohols claimed in claim 12.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18 High Holborn,
London, WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.