

Process for the preparation of predominantly
unbranched higher primary alcohols

The invention relates to a process for the preparation of predominantly unbranched higher primary alcohols by hydroformylation of olefins from the Fischer-Tropsch synthesis in the presence of water-soluble rhodium complex compounds as catalysts.

Higher, i.e. containing from 6 to 20 carbon atoms, unbranched primary alcohols are extensively used as intermediates in the chemical industry. For instance, C₆- to C₁₂-alcohols are esterified with phthalic acid to produce plasticizers distinguished by good low-temperature flexibility. Sodium salts of n-alkyl sulfates which are obtained by esterification of concentrated sulfuric acid with unbranched fatty alcohols, are biologically degraded and have consequently acquired great importance as environmentally compatible synthetic detergents. Esters based on straight-chain primary alcohols with branched dicarboxylic acids are valuable lubricants which are used, in particular, in aircraft engines.

The possibilities given above by way of example for using straight-chain primary alcohols explain the great interest in processes for their preparation which start from inexpensive raw materials and which can be carried out with great technical simplicity. A further requirement is that straight-chain feedstocks are not isomerized in the course of the preparation process and that, where it is possible for secondary and/or tertiary alcohols to form alongside primary alcohols, clear preference is given primary alcohols.

In accordance with DE-C-2 855 421, the production of dinonyl phthalate plasticizers employs C₉-alcohols which have been prepared by dimerization of butenes in the presence of organoaluminum compounds as catalysts, to give an octene mixture which is subsequently hydroformylated.

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By hydroformylation of a butene fraction, aldol condensation of the resulting aldehyde mixture and subsequent hydrogenation, C₁₀-alcohols are obtained which are processed further by the process of EP-A 0 366 089 to give
5 esters of phthalic acid.

Another route to obtaining didecyl phthalate mixtures is described in EP-A-0 424 767. The esters are prepared in a multistage process by dimerization of butene mixtures, hydroformylation and hydrogenation of the resulting
10 octene mixture to give a nonanol mixture, dehydration of the nonanol mixture to form a nonene mixture, and hydroformylation and hydrogenation of the nonene mixture to form a decanol mixture.

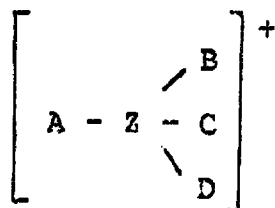
The known processes still fail to meet all of the
15 economic and technical demands made on a process carried out on the industrial scale. For instance, the starting materials are not always available in sufficient quantity or at favorable cost, or their conversion to the desired straight-chain alcohols is linked with complex processes.

20 The object was therefore to develop a process which starts from inexpensive raw materials and which produces a high yield of the desired alcohols by a simple route.

The invention consists in a process for the preparation of predominantly unbranched higher primary alcohols by
25 reacting olefins with carbon monoxide and hydrogen to give aldehydes, in liquid phase at temperatures of from 20 to 150°C and pressures of from 0.1 to 20 MPa in the presence of water and rhodium, in metallic form or as a compound, and a water-soluble phosphine as catalyst, and
30 hydrogenating the aldehydes to give alcohols. The process comprises reacting olefins obtained by Fischer-Tropsch synthesis and having from 6 to 20 carbon atoms in the molecule, or mixtures of 2 or more such olefins, in the presence of water-soluble salts whose anion is a phosphine containing at least one sulfonated or carboxylated
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aromatic radical and whose cation or cations, corresponding to the charge on the anion, is or are one or more ions of the formula



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5 in which Z is nitrogen or phosphorus, A is an alkyl or aralkyl radical having from 7 to 18 carbon atoms and B, C and D are straight-chain or branched alkyl radicals having from 1 to 4 carbon atoms.

10 The olefins used as starting material in the preparation of predominantly unbranched higher primary alcohols in accordance with the process claimed are obtained by Fischer-Tropsch synthesis. This term refers to the catalytic hydrogenation of carbon monoxide over solid catalysts, which proceeds with the construction of aliphatic molecular chains. Catalysts which have proved
15 effective are the metals iron, cobalt, nickel and ruthenium, with iron in particular having acquired importance in practice. The technical implementation of the synthesis (cf. in this respect e.g. Ullmanns Encyclopädie der technischen Chemie [Ullmann's
20 Encyclopedia of Industrial Chemistry], 4th edition (1977), volume 14, pages 329 ff.) involved the development of a series of different processes, of which two are currently in industrial use. In the "Arge process", hydrogen and carbon monoxide are reacted in fixed-bed
25 reactors at a pressure of 2.5 MPa and at temperatures of between 220 and 225°C; the "synthol process" operates with entrained-bed reactors at 2.3 MPa and 320-340°C. Irrespective of the process used, the Fischer-Tropsch synthesis is not very selective, but yields mixtures of
30 complex composition which contain saturated and unsaturated hydrocarbons of different molecular size, alcohols and, in addition, aldehydes, ketones and acids. The



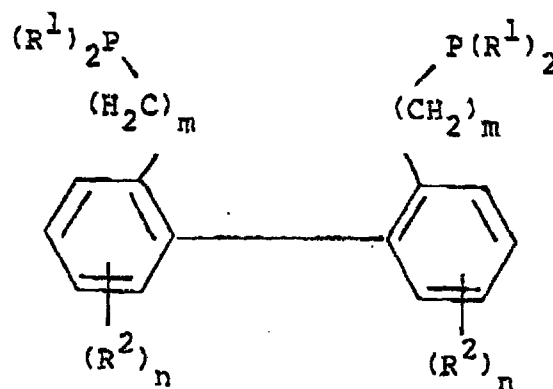
proportion of olefins in the reaction product may be up to approximately 70%, with the predominant compounds being unbranched and having from 5 to 18 carbon atoms in the molecule and a terminal double bond. The components of the reaction mixture are separated from one another in a conventional manner by distillation. The latter may be followed by a fine purification to obtain individual compounds in high purity. For example, branched hydrocarbons may be separated from their straight-chain isomers via urea inclusion compounds.

The hydroformylation of the olefins obtained as described above must be carried out under conditions which ensure that straight-chain aldehydes are formed. Consequently, the carbonyl group must be directed to the terminal carbon atom of the olefin molecule and, in addition, the double bond must retain its position in the molecule under the reaction conditions, i.e. it may not move from the terminal position to a position within the molecular chain. As a solution to this problem, it has proved particularly suitable to react the unsaturated compounds with carbon monoxide and hydrogen in a liquid two-phase system which comprises, as the organic phase, the olefin, which may be dissolved in an organic solvent, and the reaction product which is being formed and, as the aqueous phase, the catalyst solution containing the rhodium compound and water-soluble phosphine.

The water-soluble phosphines employed in the procedure according to the invention are salts whose anion is formed from a phosphine which contains at least one sulfonated or carboxylated aromatic radical. The term phosphine also includes those compounds of trivalent phosphorus in which the phosphorus atom is a component of a heterocyclic ring. The aromatic radical can be attached directly or via other groups to the phosphorus atom of the phosphine. Examples of aromatic radicals are the phenyl and the naphthyl radical. They may be mono- or polysulfonated or -carboxylated and may in addition be

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substituted by further groups of atoms or atoms, such as alkyl, hydroxyl and halogen (especially fluorine). Apart from monophosphines, polyphosphines, especially diphosphines, which contain at least one sulfonated or carboxylated aromatic radical, can also form the anion. Examples of suitable monophosphines are the triphenylphosphinemo-, di- or -trisulfonates or -carboxylates. Diphosphine anions are preferably derived from biaryl compounds of the formula

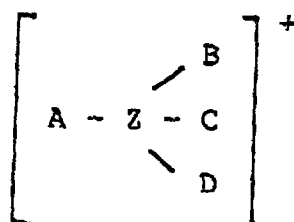


which are substituted by at least one sulfonate (SO_3^-) radical or carboxylate (COO^-) radical. In the formula, at each occurrence, R^1 is an identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radical, R^2 is identical or different and is hydrogen, an alkyl or alkoxy radical having from 1 to 14 carbon atoms, or is a cycloalkyl, aryl or aroxy radical having from 6 to 14 carbon atoms, or a fused-on benzene ring, m is identical or different and is an integer from 0 to 5, and n is likewise identical or different and is an integer from 0 to 4. Proven representatives of this class of compound are the products obtained by sulfonation of 2,2'-bis-(diphenylphosphinomethyl)-1,1'-biphenyl or 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl. One example of the anion of a heterocyclic phosphorus compound which can be mentioned is 3,4-dimethyl-2,5,6-tris(p-sulfonato-phenyl)-1-phosphanorbornadiene.

As a cation, the salts contain - corresponding to the charge on the anion - at least one ion of the formula

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in which Z is nitrogen or phosphorus, A is an alkyl or aralkyl radical having from 7 to 18 carbon atoms and B, C and D are straight-chain or branched alkyl radicals having from 1 to 4 carbon atoms.

- 5 Examples of cations of the structure mentioned which are suitable for carrying out the novel process are the trimethylcetylammmonium, trimethyldodecylammmonium, tri-
butyldodecylammmonium, dodecylethyldimethylammmonium, triethylbenzylammmonium, trimethyltetradecylphosphonium
10 and tributylhexadecylphosphonium ions.

The onium compounds used as a catalyst component according to the novel process promote the solubility of the organic substrate in the aqueous phase and hence contribute to increasing the degree of conversion. Their
15 extremely low solubility in the organic phase means that they themselves, and the metal component of the catalyst system, are discharged from the reaction zone with the reaction product either not at all or only in an amount which is so small as to be negligible. It is therefore
20 unnecessary for working up to include a separate step for recovery of rhodium from the aldehyde.

It is particularly important that, when using the water-soluble phosphines in the procedure claimed, the olefins employed in accordance with the invention are hydro-
25 formylated with high activity and selectivity, with the structure of the reacted hydrocarbons being maintained, i.e. isomerization occurs not at all or only to an insignificant extent. In addition, the effect of the phosphines is that almost exclusively terminal olefins
30 are hydroformylated. The separation effect achieved by

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this results in a further reduction in the proportion of branched compounds in the end product.

5 The preparation of the salts used in the process claimed is known. The starting materials are phosphines or phosphorus heterocycles containing sulfonated or carboxylated aryl radicals. The incorporation of the sulfonate radical is carried out by established methods, by treating the starting compounds with oleum. By varying the reaction conditions, in particular the reaction time, the reaction temperature and the ratio of phosphorus compound to sulfur trioxide, the degree of sulfonation of the starting compounds can be controlled.

15 The carboxylated phosphorus compounds can be obtained by a variety of routes, for example by reacting the basic structures with carbonyl halides and, in particular, via Grignard compounds, by reaction with carbon dioxide.

20 Expediently, the compounds initially obtained from the reaction product are amine salts which are insoluble in water but soluble in organic solvents. They are subsequently converted by treatment with a quaternary ammonium or phosphonium hydroxide into the desired onium salt of the sulfonated or carboxylated triarylphosphine.

25 Reaction of the olefins with hydrogen and carbon monoxide according to the novel process is carried out at temperatures of from 20 to 150°C, in particular from 50 to 120°C, and at pressures of from 0.1 to 20 MPa, in particular from 1 to 10 MPa.

30 The catalyst added to the reaction system may be preformed. It can also, however, be prepared with equal success from the components - the rhodium or rhodium compound and the aqueous solution of the quaternary ammonium or phosphonium salt of the phosphine containing sulfonated or carboxylated aromatic radicals - under reaction conditions in the reaction mixture, i.e. in the



presence of the olefins. In addition to metallic rhodium in finely divided form, the rhodium source employed may also comprise water-soluble rhodium salts such as rhodium chloride, rhodium sulfate, rhodium acetate, or compounds
5 soluble in organic media, such as rhodium 2-ethylhexanoate, or insoluble compounds such as rhodium oxides.

The rhodium concentration in the aqueous catalyst solution is from 10 to 2000 ppm by weight, based on the solution. The quaternary ammonium or phosphonium salt of
10 the sulfonated or carboxylated phosphine is employed in an amount such that from 1 to 1000 mol, preferably from 2 to 300 mol, of phosphine compound are present per mole of rhodium.

The pH of the aqueous catalyst solution should not be
15 less than 2. The solution is generally adjusted to a pH of from 2 to 13, preferably from 4 to 10.

The composition of the synthesis gas, i.e. the ratio of carbon monoxide to hydrogen, can be varied within broad limits. The synthesis gas generally employed is one in
20 which the volume ratio of carbon monoxide to hydrogen is 1:1, or one which deviates only slightly from this value.

The reaction can be carried out either batchwise or continuously.

The hydroformylation mixture is separated from the
25 catalyst solution by simple phase separation. Hydrogenation can be carried out without further pretreatment. However, it is also possible to free the aldehydes beforehand from accompanying by-products by distillation. The addition of hydrogen is carried out in a known manner
30 in the presence of catalysts. Suitable examples are hydrogenation catalysts based on nickel, chromium or copper. Conventionally, the hydrogenation temperature is between 100 and 180°C and the pressure is between 1 and 10 MPa. For purification, the alcohols are distilled.



They are especially suitable as the alcohol component in phthalic acid esters which are to be used as plasticizers, and for the production of alkylsulfonates and ester lubricants.

5 The following example illustrates the process according to the invention but does not limit it.

Example

Experiment 1: Hydroformylation

A 1 1 autoclave is charged with

10 185 g of an olefin mixture from the Fischer-Tropsch synthesis containing predominantly n-nonenes, and, as catalyst,

15 550 g of an aqueous solution containing 66 mol%
 of trisodium tri(m-sulfophenyl)phosphine
 and 33 mol% of tri(trimethyltetradecyl)-
 ammonium tri(m-sulfophenyl)phosphine,
 together with

20 5.44 ml of rhodium acetate solution (rhodium concentration: 20.21 g of Rh/l), corresponding to a content in the combined solutions of 80 mmol of P(III) and 200 ppm by weight of Rh

and, for adjusting the pH to about 6,

25 27.5 g of a buffer solution comprising 10 mol of
 Na acetate and 1 mol of glacial acetic
 acid per liter of solution.

The autoclave is flushed with nitrogen a number of times to remove oxygen. Synthesis gas (volume ratio $\text{CO}/\text{H}_2 = 1:1$) is then passed into the mixture at a pressure of 2.5 MPa and at 125°C with stirring. The reaction is



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terminated after 6 h, the autoclave is let down, and the organic phase (reaction product) is removed via a dip pipe and analyzed. The conversion of olefin is 85% and remains unchanged on repeating the reaction a number of times with the same catalyst solution.

Experiment 2: Hydrogenation

The crude product obtained according to Experiment 1 is hydrogenated in an autoclave with hydrogen in the presence of 2% by weight (based on the crude product) of a commercial nickel catalyst (60% by weight of Ni on kieselguhr as support) for 3 h at 8 MPa and at 150°C. When the reaction has ended the reaction vessel is cooled and let down, and the product is separated off from the catalyst.

Experiment 3: Purification of the crude alcohol

The crude alcohol from Experiment 2 is distilled in a 1 m column which is filled with 3 mm coils of stainless (VA) steel. An initial fraction is taken off at a head temperature of 93°C and a pressure of 6.7 kPa, and an intermediate fraction at 145°C and 6.7 kPa. The main fraction (26% by weight of the crude alcohol employed) is obtained at a head temperature of 147°C and a pressure of 6.7 kPa. The alcohol contained in the crude product is 99.7%.

Experiment 4: Esterification of the pure alcohol

2.3 mol of the isodecanol from Example 3 are reacted with 1 mol of phthalic anhydride at 135°C in the presence of 6 mmol of concentrated sulfuric acid, with the simultaneous removal of the water of reaction as an azeotrope with cyclohexane. When the reaction has ended, the sulfuric acid is neutralized with 5% strength sodium hydroxide solution, and excess alcohol is separated off by steam distillation at 135°C and 1.5 kPa. The residue is dried with nitrogen at 135°C and a pressure of from 2 to 3 kPa and then filtered. The ester is obtained as a clear liquid.

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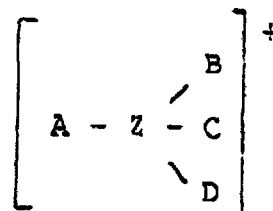
In comparison to commercial ester plasticizers whose viscosity (at 20°C) is from 120 to 130 mPa.s, the plasticizer produced using the alcohol according to the invention is distinguished by its very low viscosity of
5 64.8 mPa.s (at 20°C), which indicates the high degree of linearity of the alcohol used.

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Patent Claims

1. A process for the preparation of predominantly unbranched higher primary alcohols by reacting olefins with carbon monoxide and hydrogen to give aldehydes, in liquid phase at temperatures of from 20 to 150°C and pressures of from 0.1 to 20 MPa in the presence of water and rhodium, in metallic form or as a compound, and a water-soluble phosphine as catalyst, and hydrogenating the aldehydes to give alcohols, which comprises reacting olefins obtained by Fischer-Tropsch synthesis and having from 6 to 20 carbon atoms in the molecule, or mixtures of 2 or more such olefins, in the presence of water-soluble salts whose anion is a phosphine containing at least one sulfonated or carboxylated aromatic radical and whose cation or cations, corresponding to the charge on the anion, is or are one or more ions of the formula



in which Z is nitrogen or phosphorus, A is an alkyl or aralkyl radical having from 7 to 18 carbon atoms and B, C and D are straight-chain or branched alkyl radicals having from 1 to 4 carbon atoms.

2. The process as claimed in claim 1, wherein the anion of the water-soluble salt is derived from a mono-phosphine containing at least one sulfonated or carboxylated aromatic radical.
3. The process as claimed in claim 1, wherein the anion of the water-soluble salt is derived from a diphosphine containing at least one sulfonated or carboxylated aromatic radical.



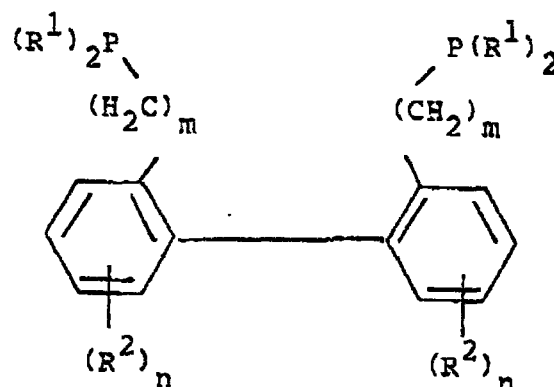


4. The process as claimed in one or more of claims 1 to 3, wherein the sulfonated or carboxylated aromatic radicals in the anion are phenyl or naphthyl radicals.

5. The process as claimed in one or more of claims 1 to 4, wherein the sulfonated or carboxylated aromatic radicals are substituted by further groups of atoms or atoms, especially fluorine.

6. The process as claimed in one or more of claims 1, 2 and 4, wherein the anions are triphenylphosphine mono-, di- or -trisulfonates or -carboxylates.

7. The process as claimed in one or more of claims 1, 3, 4 and 5, wherein the anions are biaryl compounds, substituted by at least one sulfonate radical or carboxylate radical, of the formula



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in which at each occurrence, R^1 is an identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radical, R^2 is identical or different and is hydrogen, an alkyl or alkoxy radical having from 1 to 14 carbon atoms, or is a cycloalkyl, aryl or aroxy radical having from 6 to 14 carbon atoms, or is a fused-on benzene ring, m is identical or different and is an integer from 0 to 5, and n is likewise identical or different and is an integer from 0 to 4.

8. The process as claimed in claim 7, wherein the anion

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is obtained by sulfonation of 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl or 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl.

9. The process as claimed in one or more of claims 1, 2 and 4, wherein the anion is 3,4-dimethyl-2,5,6-tris(p-sulfonatophenyl)-1-phosphanorbornadiene.

10. The process as claimed in one or more of claims 1 to 9, wherein the cation is a trimethylcetylammonium, trimethyldodecylammonium, tributyl-dodecylammonium, dodecylethyldimethylammonium, triethylbenzylammonium, trimethyltetradecylphosphonium or tributylhexadecylphosphonium ion.

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