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Process for the hydroformylation of 1,3-butadiene

5 The invention relates to a process for the hydroformylation of 1,3-butadiene with the aim of obtaining precursors of 2-propylheptanol and other valuable products.

10 Primary monohydric alcohols having 8 to 10 carbon atoms, esterified with phthalic acid, are used to a great extent as plasticizers, in particular for poly(vinyl chloride). Alcohols having shorter carbon chains give plasticizers having a good gelling power, but a disadvantage is their higher volatility. Longer-chain alcohols, as phthalic esters, lead to plasticizers which gel slowly and have poorer cold stability.

15 The properties of the phthalic ester plasticizers are determined not only by the length but also by the branching of the carbon chain in the alcohol molecule. Alcohols having a low degree of branching give ester plasticizers which are highly prized because of their high cold flexibility. Substantially linear alcohols having 8 to 10
20 carbon atoms in the molecule are therefore gaining increasing importance as alcohol component. A precondition for their use is that they are available in large amounts and inexpensively. Currently, 2-ethylhexanol is the most important alcohol component for phthalic esters.
25 However, endeavors are being made to find further raw materials as a base for the preparation of alcohols having the properties mentioned.

30 According to DE-C-2 855 421, phthalates of C₈ alcohols are used as plasticizers which are obtained by oxo-reaction of C₈ olefins, hydrogenation of the reaction product and esterification of the alcohols with phthalic anhydride. Certain demands are made of the starting olefins. They should comprise 3 to 20 % by weight of compounds having an isobutane skeleton and less than 3 %

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by weight of compounds having a quaternary carbon atom. More than 90 % by weight of the total amount of the olefins should be present as n-octenes, monomethylheptenes and dimethylhexenes. Finally, the weight ratio
5 of the total amount of n-octenes and monomethylheptenes to dimethylhexenes should be greater than 0.8.

Phthalic esters based on C_{10} alcohols are subject-matter of European Patent Application 03 66 089. The C_{10} alcohols are used in the form of a mixture which is obtained by
10 hydroformylation of a butene fraction, aldol condensation of the resulting aldehyde mixture and subsequent hydrogenation.

Another way to obtain didecyl phthalate mixtures is described in European Patent Application 04 24 767. The
15 esters are prepared by a multiple-stage process by dimerization of butene mixtures, hydroformylation and hydrogenation of the resulting octene mixture to give a nonanol mixture, dehydration of the nonanol mixture forming a nonene mixture and hydroformylation and
20 hydrogenation of the nonene mixture to give a mixture of decanols.

The known processes still do not fulfill all requirements made from the economic and technical aspect of a process carried out on the industrial scale, whether it be that
25 the starting materials are not available in sufficient quantity and/or are not available inexpensively or that the conversion of the starting material into the alcohols is connected with processes which are too complex.

The object was therefore to develop a process which,
30 starting from inexpensive raw materials, opens up a technically simple approach to the desired alcohols and, if required, further valuable materials.

The invention consists in a process for the hydroformylation of 1,3-butadiene at temperatures of 50 to 150°C and
35 pressures of 1 to 20 MPa in the presence of an aqueous

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5 solution as catalyst, which aqueous solution contains at least one water-soluble rhodium compound and at least one water-soluble organic phosphine. The process comprises reacting the butadiene at a pH in the aqueous solution of 8.0 to 11.0.

10 The starting olefin 1,3-butadiene inevitably occurs in considerable quantities in the preparation of ethylene by thermal cracking of light petroleum and higher hydrocarbons. It is isolated from the C₄ cracking cuts of the pyrolysis product, e.g. by liquid-liquid extraction with a selective solvent such as acetonitrile, dimethylformamide or n-methylpyrrolidone. In addition to this, it is easily accessible by dehydrogenation of butane or butene.

15 For the hydroformylation, 1,3-butadiene is used in the currently commercial form, i.e. in a purity of at least 99.5 % by weight. The hydroformylation of the conjugated diolefin has already been performed several times. It proceeds both under the influence of cobalt catalysts and
20 rhodium catalysts. The cobalt-catalyzed reaction is described e.g. by Adkins and Williams (J. Org. Chem. 17, 980 (1952)). It leads in moderate yield to a mixture of n- and i-valeraldehyde in a molar ratio of 1 : 1.

25 More favorable aldehyde yields are achieved in the hydroformylation of 1,3-butadiene in the presence of rhodium catalysts. Complex compounds of rhodium with a multidentate ligand which contains trivalent phosphorus atoms have proved useful. A process based on such catalysts is described, e.g., in EP-B-33 554.

30 In the context of the present invention, the hydroformylation of the 1,3-butadiene is carried out in a heterogeneous two-phase system. The principles of this process are described, e.g., in DE-C-26 27 354. The process is characterized by the introduction of an
35 organic phase, which contains the starting olefin and the

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reaction product, and an aqueous phase, in which the catalyst is dissolved. Catalysts which are used are water-soluble rhodium complex compounds with water-soluble, organic phosphines as ligands. The water-soluble phosphines include, in particular, trialkylphosphines, triarylphosphines, tri(alkyl,aryl)phosphines and alkylenediphosphines and aryldiphosphines which contain at least one organic radical substituted by a sulfonic acid group or a carboxyl group. Their preparation is known, cf. e.g. DE-C-26 27 354 and DD-A-259 194. Compounds which are particularly suitable are triphenylphosphine mono-, triphenylphosphine di- and triphenylphosphine trisulfonates which can be used as individual compounds or as a mixture of 2 or 3 sulfonate components. Surprisingly, in accordance with the new procedure, by maintaining a pH of 8.0 to 11.0 in the aqueous phase during the reaction, the selectivity of the reaction with respect to formation of C₅ aldehydes and secondary products of the C₅ aldehydes is successfully markedly increased. The secondary products of the C₅ aldehydes which occur in the course of the hydroformylation include, as intermolecular condensation products, unsaturated C₁₀ aldehydes which can be hydrogenated to form 2-propylheptanol. A further secondary product is the intramolecular condensation product of 1,6-hexanedial which, after elimination of water and addition of hydrogen, gives cyclopentanecarbaldehyde and, after hydrogenation, cyclopentanemethanol, a valuable intermediate for organic syntheses. It has proved to be particularly useful to work at pHs in the range from 8.5 to 9.5.

The pHs which are a feature of the process according to the invention relate to the aqueous phase during the reaction, that is essentially to the solution of the catalyst comprising rhodium and water-soluble organic phosphine. The pH is determined in a known manner, e.g. with the aid of a hydrogen electrode.

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The pH is adjusted by addition of basic reagents to the conventionally weakly alkaline to weakly acidic catalyst solution. Compounds which are suitable for this are alkali metal hydroxides, alkali metal carbonates, and in addition ammonia or amines. If the alkalinity of the solution exceeds the pH range to be maintained, inorganic acids, such as phosphoric acid or sulfuric acid, acid salts of polyvalent inorganic acids such as alkali metal hydrogen sulfate or water-soluble organic acids, e.g. formic acid, acetic acid, propionic acid, are added to the solution until the desired pH is achieved. It has also proved to be useful to use buffer solutions which permit a precise adjustment of the pH range and ensure its constancy over long reaction periods. Depending on the pHs required, suitable buffer mixtures are, e.g., borax-HCl, borax-NaOH, NaHCO₃-NaOH, H₃BO₃/KCl-NaOH.

The activity of the catalyst present in the alkaline solution is not impaired, although, in the opinion of those skilled in the art, the presence of rhodiumhydrido-carbonyls is decisive for the catalytic activity. Nor does the pH have any effect on the rate and extent of the reaction of butadiene. The total amount of resulting C₈ and C₁₀ aldehydes remains about the same.

Only the ratio of primary product, C₈ aldehydes, and secondary product, C₁₀ aldehydes, is shifted in favor of the C₁₀ aldehydes with increasing pH. However, when catalyst solutions having a pH of 11 and above are used, the formation of the secondary product markedly decreases.

The catalyst solution can be added preformed to the reaction system. However, with equally good results, it can also be prepared in the reaction mixture under reaction conditions from rhodium or at least one rhodium compound and the aqueous solution of at least one water-soluble organic phosphine. In addition to metallic rhodium in finely divided form, the rhodium source used



can be water-soluble rhodium salts such as rhodium chloride, rhodium sulfate, rhodium acetate or, alternatively, compounds which are sparingly soluble in water or water-insoluble such as rhodium 2-ethylhexanoate or rhodium oxides. Not only rhodium and rhodium compounds but also the water-soluble phosphines can be used as pure substances or as mixtures of two or more components.

The rhodium concentration in the aqueous catalyst solution is 20 to 2,000 ppm by weight, preferably 50 to 700 ppm by weight, based on the aqueous catalyst solution.

Per mole of rhodium, 4 to 100 mol of phosphorus are used in the form of water-soluble phosphines. Phosphine/rhodium ratios above 15 : 1 repress the formation of branched primary product and favor the production of dialdehyde. The phosphine/rhodium ratio also has an influence on the formation of C_{10} aldehydes. Below a molar ratio $P : Rh = 30 : 1$, the aldol condensation products are only formed to a slight extent. The total amount of unbranched monoaldehyde and its intermolecular aldol condensation product is scarcely influenced by the P/Rh ratio.

The hydroformylation of the 1,3-butadiene proceeds at temperatures between 60 and 150°C, preferably 90 and 120°C. Higher temperatures within the said range favor the formation of dialdehyde. Above about 120°C, the formation of C_8 aldehydes and their intermolecular aldol condensation products decreases.

The hydroformylation of 1,3-butadiene is preferably carried out at pressures of 1 to 10 MPa. Lower pressure within the said ranges preferentially leads to the formation of C_8 aldehydes, but impairs the conversion rate. Pressures above 10 MPa promote the aldol condensation.

The conversion of butadiene per unit of time and the

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condensation of C_8 aldehydes to form C_{12} aldehydes is significantly increased if a phase transfer reagent (solubilizer) is added to the aqueous alkaline catalyst solution. It alters the physical properties of the interfaces between the two liquid phases and facilitates the transfer of the organic reactants into the aqueous catalyst phase.

Compounds are known as solubilizers, the hydrophilic groups of which are ionic (anionic or cationic) or nonionic. The anionic compounds include sodium salts, potassium salts or ammonium salts of carboxylic acids having 8 to 20 carbon atoms, in particular of saturated fatty acids having 12 to 18 carbon atoms, in addition alkyl sulfates, alkylbenzenesulfonates and alkylbenzenephosphates. Examples of cationic solubilizers are tetraalkylammonium and N-alkylpyridinium salts. The nonionic phase transfer reagents cannot dissociate into ions in aqueous solution. These include alkyl polyethylene glycols, alkylphenyl polyethylene glycols, alkylolamides of fatty acids and trialkylamine oxides. Finally, ampholytes such as aminocarboxylic acids, betaines and sulfobetaines are also used as solubilizers.

In particular, cationic solubilizers of the formula $[A-N(R^1R^2R^3)]^+E^-$ have proved useful, in which A is a straight-chain or branched alkyl radical having 6 to 25 carbon atoms, R^1 , R^2 , R^3 are identical or different and are straight-chain or branched alkyl radicals having 1 to 5 carbon atoms and E is an anion, in particular sulfate, tetrafluoroborate, acetate, methosulfate, benzenesulfonate, alkylbenzenesulfonate, toluenesulfonate, lactate or citrate.

The reaction mixture arising in the hydroformylation is separated from the catalyst by simple phase separation. The aqueous catalyst solution can, if required after regeneration and adjustment of the rhodium and/or phosphine concentration, be reused. The organic phase is



divided by distillation into the constituents which are used as such or further processed. The C_{10} aldehyde fraction can be hydrogenated directly to form 2-propylheptanol. The C_8 aldehydes are preferably converted to aldols as a mixture. The reaction proceeds in a conventional manner under the influence of basic catalysts. Catalysts which are used are alkali metal carbonates or alkali metal hydroxides, in particular compounds of sodium or of potassium and amines, preferably tertiary amines, such as triethylamine, tri-n-propylamine, tri-n-butylamine. Temperatures of 60 to 160°C, in particular 80 to 130°C, and atmospheric pressure or elevated pressure up to about 1 MPa are employed. The reaction time is a few minutes up to several hours and is dependent, in particular, on catalyst type and reaction temperature. Because of their relatively high reaction rate, n- C_8 aldehydes, especially, dimerize with themselves or with isomeric C_8 aldehydes to give C_{10} aldehydes; in contrast, condensation of the branched C_8 aldehydes among themselves proceeds completely in the background. The isomeric C_{10} aldehydes are hydrogenated to give the corresponding saturated alcohols. Hydrogenation catalysts which are suitable for this reaction are those 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. The mixture of isomeric C_{10} alcohols is distilled to purify it. Independently of their origin, directly from the hydroformylation stage or from the aldol condensation of the C_8 aldehydes, they are very highly suitable as alcohol component in phthalic esters which are used as plasticizers. The preparation of phthalic esters is known [cf. Ullmann, Encyclopädie der Technischen Chemie [Encyclopaedia of Industrial Chemistry] (1979), Vol. 18, page 536 ff.]. Phthalic anhydride is expediently reacted with the decyl alcohol mixture in a single stage in a molar ratio 1 : 2. The reaction rate can be increased by catalysts and/or by increasing the reaction temperature. In order to shift the equilibrium in the direction of ester formation it is necessary to

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remove from the reaction mixture the water formed.

The following examples describe the invention, but it is not restricted to the embodiments described.

The procedure is carried out in all examples in the same manner. Into a 125 ml stainless steel autoclave are introduced, in an argon atmosphere, 40 g of an aqueous catalyst solution which contains 16.4 mg of rhodium (in the form of rhodium 2-ethylhexanoate or rhodium sulfate equivalent to 410 ppm of Rh) and variable amounts of tris(m-sulfonatophenyl)phosphine trisodium salt and the pH thereof, if not stated otherwise, is adjusted by respective addition of sodium carbonate or sulfuric acid. The catalyst solution is treated at 110°C and 10 MPa for 90 min with synthesis gas (volume ratio CO/H₂ = 1 : 1). 20 g of 1,3-butadiene are added in each case to the preformed catalyst, the desired reaction pressure is adjusted using synthesis gas and the mixture is allowed to react for 12 h. After completion of the reaction, catalyst and product phase are separated. The catalyst phase is extracted three times, each time with 15 ml of ether. Product phase and ether extract are combined, dried by sodium sulfate and hydrogenated at 140°C and 20 MPa for 12 h in the presence of a Pt-activated charcoal catalyst (10 % by weight of Pt). The hydrogenation product is analyzed by gas chromatography.

In the examples, the following abbreviations are used:

n-pentanol	n-P
2-methylbutanol	2-MB
cyclopentanemethanol	CPM
2-propylheptanol	PH

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Example 1

Reaction conditions: 120°C; 20 MPa; aqueous/organic phase (by vol.) = 2 : 1; CO/H₂ (by vol.) = 1 : 1; pH of the

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aqueous phase: 9.

Experiment	P:Rh (in moles)	n-P (% by weight)	2-MB (% by weight)	CPM (% by weight)	PH (% by weight)	(n-P+PH) (% by weight)
1/1	15:1	45	4	7	9	54
1/2	30:1	48	5	9	10	58
1/3	40:1	48	4	8	13	61
1/4	60:1	38	4	7	20	58
1/5	80:1	42	3	8	18	60

Example 2

Reaction conditions: 120°C; 20 MPa; P/Rh (in moles) =
 60 : 1; aqueous/organic phase (by vol.) = 2 : 1; CO/H₂
 (by vol.) = 1 : 1.

Experiment	pH	n-P (% by weight)	2-MB (% by weight)	CPM (% by weight)	PH (% by weight)	(n-P+PH) (% by weight)
2/1	3	61	4	8	7	68
2/2	7	47	3	9	8	55
2/3	9	36	3	8	23	60
2/4	11	55	4	8	11	66

Example 3

Reaction conditions: 20 MPa; P/Rh (in moles) = 60 : 1;
 aqueous/organic phase (by vol.) = 2 : 1; CO/H₂ (by vol.)
 = 1 : 1; pH of the aqueous phase: 9.

Experiment	Tempera- ture (°C)	n-P (% by weight)	2-MB (% by weight)	CPM (% by weight)	PH (% by weight)	(n-P+PH) (% by weight)
3/1	100	31	2	5	27	58
3/2	120	36	3	8	23	59
3/3	140	29	3	8	7	36

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Example 4

Reaction conditions: 120°C; P/Rh (in moles) = 60 : 1;
aqueous/organic phase (by vol.) = 2 : 1; pH of the
aqueous phase: 9.

5	Experiment	Pressure (MPa)	n-P (% by weight)	2-MB (% by weight)	CPM (% by weight)	PH (% by weight)	(n-P+PH) (% by weight)
	4/1	4.0	57	2	12	8	65
	4/2	6.0	67	4	10	10	77
	4/3	8.0	55	3	9	13	68
	4/4	12.0	49	4	8	18	67
10	4/5	16.0	28	2	6	23	51
	4/6	20.0	36	3	8	23	59
	4/7	26.0	52	3	8	15	67

Example 5

Reaction conditions: 100°C; 5.5 MPa; P/Rh (in moles) =
15 60 : 1; aqueous/organic phase (by vol.) = 2 : 1; CO/H₂
(by vol.) = 1 : 1.

	Experiment	pH	n-P (% by weight)	2-MB (% by weight)	CPM (% by weight)	PH (% by weight)	(n-P+PH) (% by weight)
	5/1	9	33	2	4	25	58
	5/2	9	26	2	4	32	58
20	5/3	11	49	2	1	19	68
	5/4	11	53	2	1	22	75

The results of these experiments show that the selec-
tivity of the reaction for the aldolization product
2-propylheptenal is satisfactorily high even at pressures
25 around 5 MPa. The selectivity for the aldol condensation
product decreases on transferring from the weakly
alkaline to the more strongly alkaline region.

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Example 6

Reaction conditions: 100°C; 5.5 MPa; P/Rh (in moles) = 60 : 1; aqueous/organic phase (by vol.) = 2 : 1; CO/H₂ (by vol.) = 1 : 1; pH of the aqueous phase: 9 (adjusted in Experiments 6/2 to 6/4 with the aid of an H₃BO₃/KCl-NaOH buffer); DTAB: dodecyltrimethylammonium bromide.

Experiment	Surfactant	Buffer	n-P (% by weight)	2-MS (% by weight)	CFM (% by weight)	PH (% by weight)	(n-P+PH) (% by weight)
6/1	DTAB	-	24	2	8	20	44
6/2	-	+	27	2	4	19	46
6/3	-	+	32	2	5	18	50
6/4	DTAB	+	22	3	7	29	51

The results show that the selectivity of the reaction with respect to formation of linear C₈ aldehyde and its aldol condensation secondary product decreases if the procedure is carried out with the addition of surfactant or buffer mixtures.

The experiments below show the increases of the conversion/unit of time when a surfactant is added to the catalyst solution

Reaction time/h	Pressure drop / MPa	
	without surfactant	with addition of surfactant
1	0.7	2.0
2	1.3	3.1
4	2.8	4.9
8	4.3	6.0
12	5.1	6.3

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Example 7 (comparison)

5 This comparative example shows that 1-butene behaves completely differently from 1,3-butadiene in the hydroformylation under the conditions according to the invention. The hydrogenated reaction product chiefly comprises n-pentanol and only contains 2-propylheptanol in very minor amounts.

10 Reaction conditions: 100°C; 5.5 MPa; P/Rh (in moles) = 60 : 1; aqueous/organic phase (by vol.) = 2 : 1; CO/H₂ (by vol.) = 1 : 1; pH of the aqueous phase: 9.

Experiment	n-P (% by weight)	2-MB (% by weight)	PH (% by weight)
7/1	91	4	1
7/2	93	4	0.4

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Patent claims

- 1.) A process for the hydroformylation of 1,3-butadiene at temperatures of 60 to 150°C and pressures of 1 to 20 MPa in the presence of an aqueous solution as catalyst which contains at least one water-soluble rhodium compound and at least one water-soluble organic phosphine, which comprises reacting the butadiene at a pH in the aqueous solution of 8.0 to 11.0.
- 2.) The process as claimed in claim 1, wherein the pH in the aqueous solution is 8.5 to 9.5.
- 3.) The process as claimed in claim 1 or 2, wherein the pH is adjusted with the aid of a buffer mixture.
- 4.) The process as claimed in one or more of claims 1 to 3, wherein the reaction proceeds at temperatures of 90 to 120°C.
- 5.) The process as claimed in one or more of claims 1 to 4, wherein the reaction is carried out at pressures of 1 to 10 MPa.
- 6.) The process as claimed in one or more of claims 1 to 5, wherein the rhodium concentration in the aqueous catalyst solution is 20 to 2000 ppm by weight, preferably 50 to 700 ppm by weight, based on the aqueous catalyst solution.
- 7.) The process as claimed in one or more of claims 1 to 6, wherein, per mole of rhodium, 4 to 100 mol of phosphorus, preferably 10 to 60 mol of phosphorus, are present in the aqueous solutions.
- 8.) The process as claimed in one or more of claims 1 to 7, wherein the water-soluble phosphines used are triarylphosphines, trialkylphosphines, tri(alkyl-

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aryl)phosphines, alkylendiphosphines or aryldiphosphines containing at least one sulfonic acid group or at least one carboxyl group.

- 9.) The process as claimed in one or more of claims 1 to 8, wherein the aqueous solution contains a solubilizer.



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