

Method for separating 1-butene from C₄-containing hydrocarbon streams by hydroformylation

The present invention relates to the selective hydroformylation of 1-butene to
5 valeraldehyde from C₄-containing hydrocarbon streams which comprise both
1-butene and isobutene.

Isobutene is frequently present in industrial streams together with saturated and
unsaturated C₄ hydrocarbons. Owing to the small boiling point difference and/or the
10 very low separation factor between isobutene and 1-butene, isobutene cannot be
removed economically from these mixtures by distillation. Isobutene is therefore
typically obtained from industrial hydrocarbon mixtures by converting isobutene to a
derivative which can be removed easily from the remaining hydrocarbon mixture, and
by dissociating the isolated derivative to isobutene and derivatizing agent.

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Isobutene is the starting material for the preparation of a multitude of products, for
example for the preparation of butyl rubber, polyisobutylene, isobutene oligomers,
branched C₅ aldehydes, C₅ carboxylic acids, C₅ alcohols and C₅ olefins. In addition, it
is used as an alkylating agent, especially for the synthesis of tert-butyl aromatics, and
20 as an intermediate for the production of peroxides. In addition, isobutene can be
used as a precursor for the preparation of methacrylic acid and esters thereof.

Typically, isobutene is removed from C₄ cuts, for example the C₄ fraction of a
steamcracker, as follows:

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After removal of the majority of the polyunsaturated hydrocarbons, principally
butadiene, by extraction/extractive distillation or selective hydrogenation (SHP) to
linear butenes, the remaining mixture (raffinate I or selectively hydrogenated crack-
C₄) is reacted with alcohol or water. Isobutene forms methyl tert-butyl ether (MTBE)
30 in the case of use of methanol, ethyl tert-butyl ether (ETBE) in the case of ethanol,
and tert-butanol (TBA) in the case of use of water. On completion of derivatization
and removal, all three products can be dissociated to isobutene in a reversal of their

formation. For the isolation of isobutene, as well as various separating operations, at least two reaction stages are accordingly required.

Alternatively, isobutene can be removed from a C₄ hydrocarbon stream which typically contains less than 1% by mass of butadiene (C₄ stream from fluid catalytic cracking processes, raffinate I or selectively hydrogenated crack-C₄), in the following manner:

The starting mixture is hydrogenated and isomerized, i.e. butadiene (still) present is selectively hydrogenated down to a residual content of below 5 ppm by mass, and 1-butene is simultaneously isomerized to 2-butenes. The equilibrium position between 1-butene and the isomeric 2-butenes is, for example at 80°C, at a ratio of 1 : 17.

When the isomerization is performed in a reactive distillation, a virtually 1-butene-free top product can be removed, from which pure isobutene can be worked up further. The bottom product obtained is an isobutene-free mixture of 2-butenes. However, a disadvantage is that the isobutene has a lower purity than the product prepared by the method of derivatization. Moreover, 1-butene is converted to the less reactive and also economically less attractive 2-butenes.

A further alternative consists in exploiting the higher reactivity of 1-butene compared to isobutene in the hydroformylation, in order to selectively remove 1-butene from the mixture by hydroformylation. However, the reactivity differences of 1-butene and isobutene are generally too low to achieve selectivities of commercial interest. EP 0 016 286 presents a process with which 1-butene can be converted selectively to valeraldehyde in the presence of isobutene. In the process described there, however, an at least 100-fold excess of phosphine ligand is required in order to achieve the desired selectivities, which again makes the process unattractive.

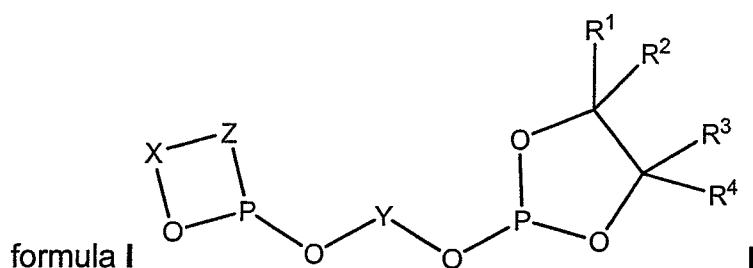
International application WO 2005/028404 makes use of the same process in its examples. This also claims, without specifying experimental details, achievement of

not more than 5% isobutene conversion at 65% 1-butene conversion with the ligands A described there.

However, a 65% 1-butene conversion can in no way be considered to be sufficient to satisfactorily solve the technical problem of separating 1-butene and isobutene. A technical solution should lower the 1-butene content well below the thermodynamic equilibrium between 1-butene and the isomeric 2-butene, in order subsequently to be able to distil off isobutene freed of 1-butene. A minimum requirement can be considered to be a 1-butene conversion of 95% with not more than 5% isobutene conversion. Preference is given to a 1-butene conversion of at least 99% at an isobutene conversion of not more than 5%.

The technical problem was therefore to develop a process with which 1-butene can be hydroformylated selectively from a C₄-containing hydrocarbon mixture which comprises isobutene and 1-butene and may comprise 2-butenes, without isobutene also reacting in the same way. Ideally, 2-butenes which are optionally present are hydroformylated or isomerized to a minimum degree, such that the end concentration of 1-butene is considerably below the concentration of 1-butene in the thermodynamic equilibrium between 1-butene and 2-butenes. A minimum requirement can be considered to be a 1-butene conversion of 95% at not more than 5% isobutene conversion. 1-Butene shall be hydroformylated with an n/iso selectivity of at least 97% at the terminal carbon atom to give n-valeraldehyde. The process shall need considerably lower ligand excesses than EP 0 016 286.

This problem has been solved by a process for removing 1-butene from C₄-containing hydrocarbon mixtures comprising isobutene and 1-butene by hydroformylation, the catalyst system used consisting of one or the transition metals of groups 8 to 10, preferably rhodium, and a bisphosphite ligand of the following



where X

= divalent substituted or unsubstituted bisalkylene or bisarylene radical which contains one or more heteroatom(s), Y = divalent substituted or unsubstituted bisarylene or bisalkylene radical which contains one or more heteroatom(s), Z = oxygen or NR⁹, and R¹, R², R³, R⁴ are identical or different, substituted or unsubstituted, connected, unconnected or fused aryl or heteroaryl radicals, and R⁹ = hydrogen or substituted or unsubstituted alkyl or aryl radical which contains one or more heteroatom(s), the bisphosphite ligand of the above-specified formula I being used in an excess of a molar ratio of 100 : 1 to 1 : 1 relative to the transition metal, and less than 5% of the isobutene present being converted at a 1-butene conversion of more than 95%.

It has now been found that, from a C₄-containing hydrocarbon mixture comprising isobutene and 1-butene, the 1-butene can be converted by hydroformylation at temperatures below 120°C, preferably below 100°C, to C₅ aldehydes from the hydrocarbon mixture to an extent of more than 99% by weight, the conversion of the isobutene present being less than 5% by weight, when a catalyst system consisting of rhodium and a bisphosphite, described in DE 10 2006 058682, is used and the reaction temperature is below 100°C. Subsequently, the hydroformylation mixture is preferably separated into a C₅ aldehyde fraction, pure isobutene, into a catalyst fraction and into a fraction comprising the remaining hydrocarbons, the C₅ aldehyde fraction consisting of valeraldehyde with an n/iso selectivity of more than 97%.

The process according to the invention has the following advantages: with only one chemical reaction and a distillative workup, two sought-after intermediates are obtained from a C₄ hydrocarbon mixture comprising isobutene and 1-butene, specifically isobutene and the C₅ aldehyde mixture with a high proportion of valeraldehyde. In addition, any hydrocarbon mixture comprising the isomeric 2-butenes obtained can be utilized for further reactions, for example for the preparation of oligomers or C₅ aldehydes.

Feedstocks for the process according to the invention are, for example, light petroleum fractions from refineries, C₄ fractions from cracking plants (for example

steamcrackers, hydrocrackers, catcrackers), mixtures from Fischer-Tropsch syntheses, mixtures formed by metathesis of olefins, mixtures which are obtained by dehydrogenating saturated hydrocarbons, and mixtures which arise from methanol (or other oxygenates) to olefin (MTO) processes. These techniques are described in the technical literature (H. J. Arpe, Industrielle Organische Chemie [Industrial Organic Chemistry], Wiley-VCH, 6th Edition, 2007, pages 9 – 12, 23, 36, 93 – 97, 120).

Preferred feedstocks among those mentioned above are C₄ fractions from steamcrackers, which are operated primarily for production of ethene and propene and in which the raw materials used are, for example, refinery gases, naphtha, gas oil, LPG (liquefied petroleum gas) and NGL (natural gas liquid), C₄ fractions from catcrackers or products from butane dehydrogenation plants. According to the process, the C₄ cuts obtained as by-products contain different proportions of 1,3-butadiene, 1-butene, Z-2-butene, E-2-butene, isobutene, n-butane and isobutane.

For the process according to the invention, it is advantageous to remove polyunsaturated hydrocarbons, such as 1,3-butadiene, from the feed mixture. This can be done by known processes, for example by extraction, extractive distillation or complex formation (cf. H. J. Arpe, Industrielle Organische Chemie, Wiley-VCH, 6th Edition, 2007, pages 118 – 119).

An alternative to the removal of the polyunsaturated hydrocarbons is a selective chemical conversion. For example, 1,3-butadiene can be hydrogenated selectively to linear butenes, as described, for example, in EP 0 523 482. The 1,3-butadiene can also be removed at least partially by selective conversions of the 1,3-butadiene, for example dimerization to cyclooctadiene, trimerization to cyclododecatriene, polymerization or telomerization reactions. When a crack-C₄ cut has been used as the raw material, what remains in all cases is a hydrocarbon mixture (e.g. raffinate I or hydrogenated crack-C₄ (HCC₄)), which comprises principally the saturated hydrocarbons, n-butane and isobutane, and the olefins, isobutene, 1-butene and 2-butenes.

Typical compositions of C₄ cuts from which the majority of the polyunsaturated hydrocarbons have been removed and which can be used in the process according to the invention are listed in Table 1 below.

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Table 1

Component	Steamcracker		Steamcracker		Catcracker	
	HCC ₄	HCC ₄ /SHP	Raff. I	Raff. I/SHP	CC ₄	CC ₄ /SHP
isobutane [% by mass]	1 - 4.5	1 - 4.5	1.5 - 8	1.5 - 8	37	37
n-butane [% by mass]	5 - 8	5 - 8	6 - 15	6 - 15	13	13
E-2-butene [% by mass]	18 - 21	18 - 21	7 - 10	7 - 10	12	12
1-butene [% by mass]	35 - 45	35 - 45	15 - 35	15 - 35	12	12
isobutene [% by mass]	22 - 28	22 - 28	33 - 50	33 - 50	15	15
Z-2-butene [% by mass]	5 - 9	5 - 9	4 - 8	4 - 8	11	11
1,3-butadiene [ppm by mass]	500 - 8000	0 - 50	50 - 8000	0 - 50	< 10000	0 - 50

Explanation

- HCC₄: typical of a C₄ mixture which is obtained from the crack-C₄ of a steamcracker (high severity) after the hydrogenation of the 1,3-butadiene without additional moderation of the catalyst.
- HCC₄/SHP: HCC₄ composition in which residues of 1,3-butadiene have been reduced further in a SHP.
- Raff. I (raffinate I): typical of a C₄ mixture which is obtained from the crack-C₄ of a steamcracker (high severity) after the removal of the 1,3-butadiene, for example by an NMP extractive rectification.
- Raff. I/SHP: Raff. I composition in which residues of 1,3-butadiene have been

reduced further in an SHP.

- CC₄: typical composition of a crack-C₄ which is obtained from a catcracker.
- CC₄/SHP: CC₄ composition in which residues of 1,3-butadiene have been reduced further in an SHP.

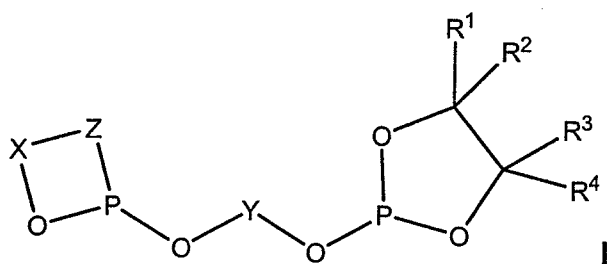
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The hydroformylation of the feed hydrocarbon mixture comprising isobutene and 1-butene is effected under conditions under which the 1-butene present in the feed mixture is converted to an extent of more than 95%, and the isobutene present in the feed mixture to an extent of less than 5%. Preferably, the 1-butene present in the feed mixture is converted to an extent of more than 99% and the isobutene present in the feed mixture to an extent of less than 5%. More preferably, the 1-butene is hydroformylated with an n/iso selectivity of more than 97%.

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For the selective hydroformylation, preference is given to using catalyst systems consisting of rhodium and bisphosphites of the general formula I:

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where

X = divalent substituted or unsubstituted bisalkylene or bisarylene radical which contains one or more heteroatom(s),

20

Y = divalent substituted or unsubstituted bisarylene or bisalkylene radical which contains one or more heteroatom(s),

Z = oxygen or NR⁹,

R¹, R², R³, R⁴ are identical or different, substituted or unsubstituted, connected,

unconnected, fused or unfused aryl or heteroaryl radicals,

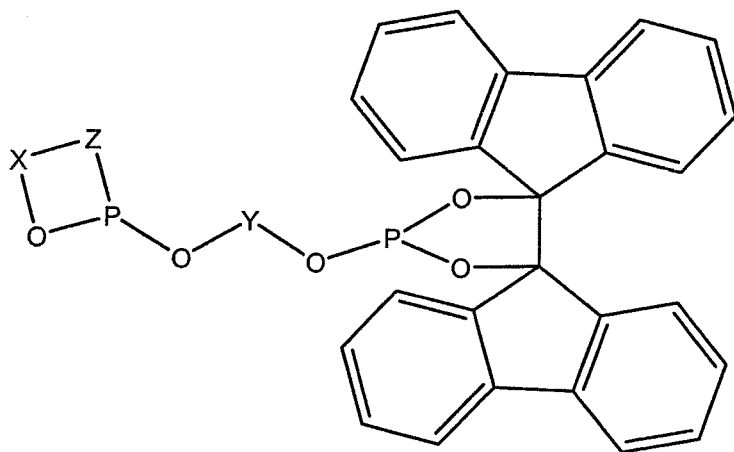
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and R⁹ = hydrogen or substituted or unsubstituted alkyl or aryl radical which contains one or more heteroatom(s). The R¹, R², R³, R⁴, R⁹, X or Y radicals may be

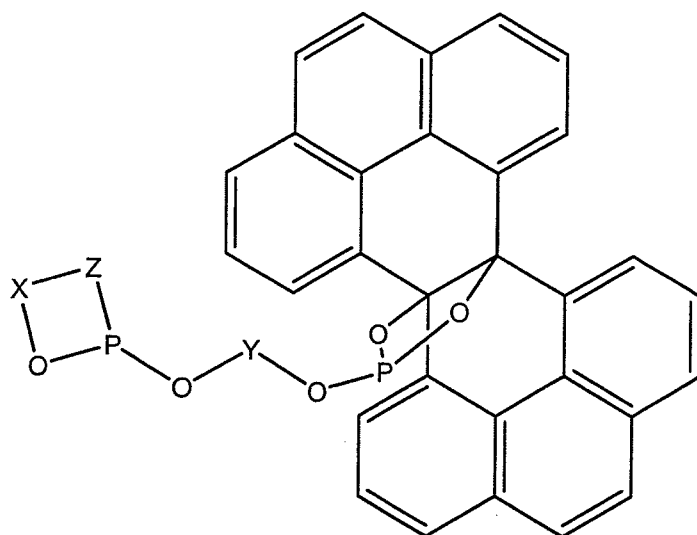
substituted, for example, by at least one radical selected from aliphatic, alicyclic,

aromatic, heteroaromatic, mixed aliphatic-alicyclic, mixed aliphatic-aromatic, heterocyclic, mixed aliphatic-heterocyclic hydrocarbon radicals having 1 to 50 carbon atoms, F, Cl, Br, I, $-\text{CF}_3$, $-(\text{CH}_2)_i(\text{CF}_2)_j\text{CF}_3$ where $i = 0 - 9$ and $j = 0 - 9$, $-\text{SiR}^{21}_3$, $-\text{Si}(\text{OR}^{21})_3$, $-\text{SiR}^{21}(\text{OR}^{21})_2$, $-\text{SiR}^{21}_2\text{OR}^{21}$, $-\text{OSiR}^{21}_3$, $-\text{OSi}(\text{OR}^{21})_3$, $-\text{OSiR}^{21}(\text{OR}^{21})_2$, $-\text{OSiR}^{21}_2\text{OR}^{21}$, $-\text{OR}^{19}$, $-\text{COR}^{19}$, $-\text{CO}_2\text{R}^{19}$, $-\text{CO}_2\text{M}$, $-\text{SO}_2\text{R}^{19}$, $-\text{SOR}^{19}$, $-\text{SO}_3\text{R}^{19}$, $-\text{SO}_3\text{M}$, $-\text{SO}_2\text{NR}^{19}\text{R}^{20}$, $-\text{NR}^{19}\text{R}^{20}$, or $-\text{N}=\text{CR}^{19}\text{R}^{20}$, where R^{19} , R^{20} and R^{21} are each independently selected from H, monovalent substituted or unsubstituted aliphatic and aromatic hydrocarbon radicals having 1 to 25 carbon atoms, but excluding $\text{R}^{21} = \text{H}$, and M is an alkali metal, alkaline earth metal, ammonium or phosphonium ion.

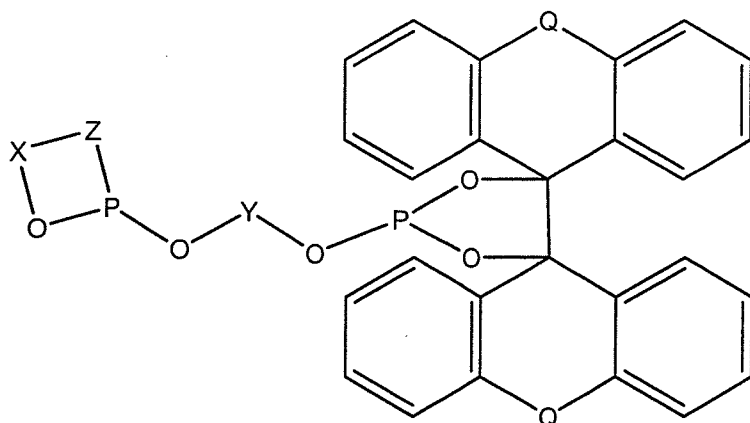
- 10 Preferred substituents, especially for X and Y radicals, are tert-butyl and methoxy groups. The R^1 , R^2 , R^3 , R^4 radicals are preferably unsubstituted phenyl radicals. Such radicals may, for example, be those as are present in the formulae I-1, I-2 or I-3.



I-1



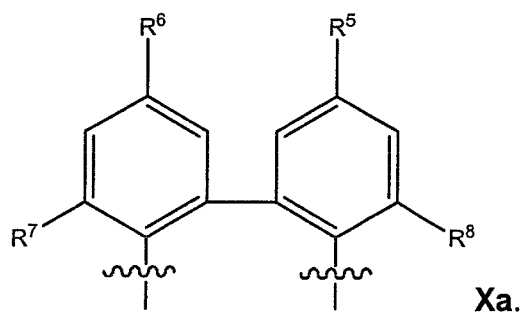
I-2

**I-3**

where Q, for example, may be the same or different and may be CH_2 , CR^9R^{10} , CHR^9 , O, NH or NR^9 , where R^9 and R^{10} may be the same or different and may each be as defined above for R^9 .

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In the bisphosphite, the X radical may also be an **Xa** radical



The R^5 , R^6 , R^7 , R^8 radicals may each independently be substituted or unsubstituted aliphatic, alicyclic, aromatic, heteroaromatic, mixed aliphatic-alicyclic, mixed aliphatic-aromatic, heterocyclic, mixed aliphatic-heterocyclic hydrocarbon radicals having 1 to 50 carbon atoms or H, F, Cl, Br, I, $-\text{CF}_3$, $-(\text{CH}_2)_i(\text{CF}_2)_j\text{CF}_3$ where $i = 0 - 9$ and $j = 0 - 9$, $-\text{SiR}^{21}_3$, $-\text{Si}(\text{OR}^{21})_3$, $-\text{SiR}^{21}(\text{OR}^{21})_2$, $-\text{SiR}^{21}_2\text{OR}^{21}$, $-\text{OSiR}^{21}_3$, $-\text{OSi}(\text{OR}^{21})_3$, $-\text{OSiR}^{21}(\text{OR}^{21})_2$, $-\text{OSiR}^{21}_2\text{OR}^{21}$, $-\text{OR}^{19}$, $-\text{COR}^{19}$, $-\text{CO}_2\text{R}^{19}$, $-\text{CO}_2\text{M}$, $-\text{SO}_2\text{R}^{19}$, $-\text{SOR}^{19}$, $-\text{SO}_3\text{R}^{19}$, $-\text{SO}_3\text{M}$, $-\text{SO}_2\text{NR}^{19}\text{R}^{20}$, $-\text{NR}^{19}\text{R}^{20}$, or $-\text{N}=\text{CR}^{19}\text{R}^{20}$, where R^{19} , R^{20} and R^{21} are each independently selected from H, monovalent substituted or unsubstituted aliphatic and aromatic hydrocarbon radicals having 1 to 25 carbon atoms, but excluding $\text{R}^{21} = \text{H}$, and M is an alkali metal, alkaline earth metal, ammonium or phosphonium ion.

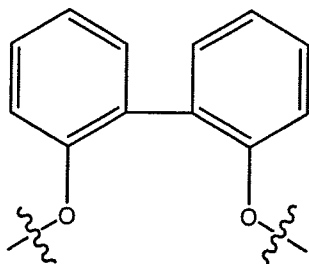
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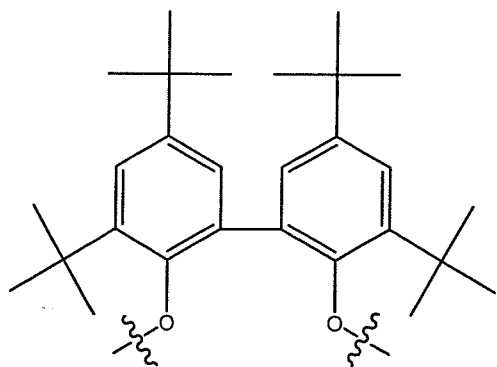
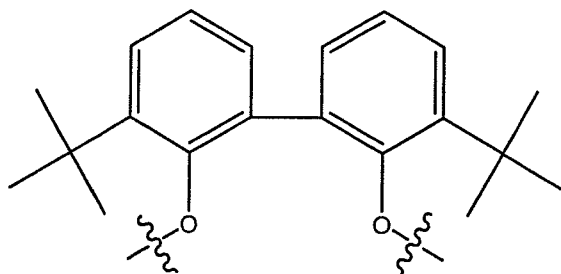
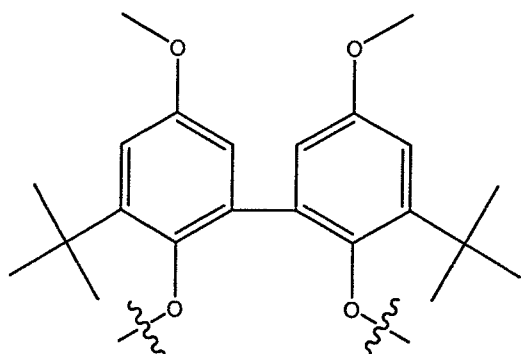
The R^5 , R^6 , R^7 , R^8 radicals may, for example, be substituted by one or more radicals

selected from aliphatic, alicyclic, aromatic, heteroaromatic, mixed aliphatic-alicyclic, mixed aliphatic-aromatic, heterocyclic, mixed aliphatic-heterocyclic hydrocarbon radicals having 1 to 50 carbon atoms, F, Cl, Br, I, $-\text{CF}_3$, $-(\text{CH}_2)_i(\text{CF}_2)_j\text{CF}_3$ where $i = 0 - 9$ and $j = 0 - 9$, $-\text{SiR}^{21}_3$, $-\text{Si}(\text{OR}^{21})_3$, $-\text{SiR}^{21}(\text{OR}^{21})_2$, $-\text{SiR}^{21}_2\text{OR}^{21}$, $-\text{OSiR}^{21}_3$,
 5 $-\text{OSi}(\text{OR}^{21})_3$, $-\text{OSiR}^{21}(\text{OR}^{21})_2$, $-\text{OSiR}^{21}_2\text{OR}^{21}$, $-\text{OR}^{19}$, $-\text{COR}^{19}$, $-\text{CO}_2\text{R}^{19}$, $-\text{CO}_2\text{M}$, $-\text{SO}_2\text{R}^{19}$, $-\text{SOR}^{19}$, $-\text{SO}_3\text{R}^{19}$, $-\text{SO}_3\text{M}$, $-\text{SO}_2\text{NR}^{19}\text{R}^{20}$, $-\text{NR}^{19}\text{R}^{20}$, or $-\text{N}=\text{CR}^{19}\text{R}^{20}$, where R^{19} , R^{20} , R^{21} and M may each be as defined above. In the **Xa** radical, the R^5 to R^8 radicals are preferably each hydrogen, alkoxy groups, especially methoxy groups, or tert-butyl groups. Preferably, the R^5 and R^6 radicals and the R^7 and R^8 radicals are
 10 each identical pairs. More preferably the R^5 and R^6 radicals are methoxy groups and/or the R^7 and R^8 radicals are tert-butyl groups.

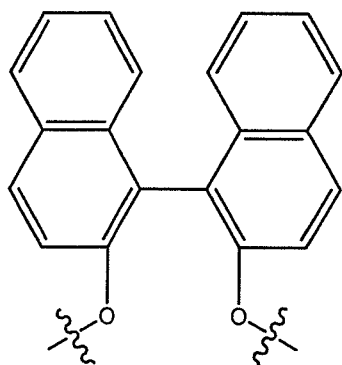
The X in the bisphosphite is preferably an ethylene radical substituted by $\text{R}^{1'}$, $\text{R}^{2'}$, $\text{R}^{3'}$ and $\text{R}^{4'}$ radicals, where the $\text{R}^{1'}$, $\text{R}^{2'}$, $\text{R}^{3'}$ and $\text{R}^{4'}$ radicals may be identical or different,
 15 substituted or unsubstituted, connected, unconnected or fused aryl or heteroaryl radicals. Possible substituents for the $\text{R}^{1'}$ to $\text{R}^{4'}$ radicals are the substituents specified for the R^1 to R^4 radicals. Particularly preferred bisphosphites are those which are symmetrical, i.e. those in which X is an ethylene radical substituted by the $\text{R}^{1'}$, $\text{R}^{2'}$, $\text{R}^{3'}$ and $\text{R}^{4'}$ radicals, where the R^1 and $\text{R}^{1'}$, R^2 and $\text{R}^{2'}$, R^3 and $\text{R}^{3'}$ and R^4 and $\text{R}^{4'}$ radicals
 20 are each identical.

The divalent Y radical in the inventive bisphosphite may preferably be a substituted or unsubstituted bisphenyl radical or bisnaphthyl radical. Possible substituents may be the abovementioned substituents. The Y radical is preferably selected from the
 25 bisphenoxy radicals of the formulae **IIa** to **IId**

**IIa**

**IIb****IIc****IIId**

or bisnaphthoxy radicals of the formula **III**

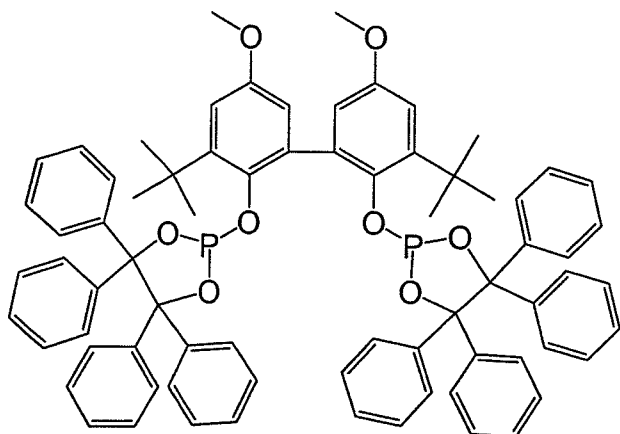
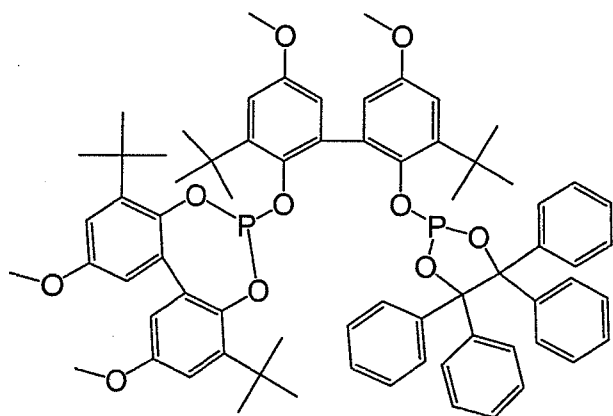
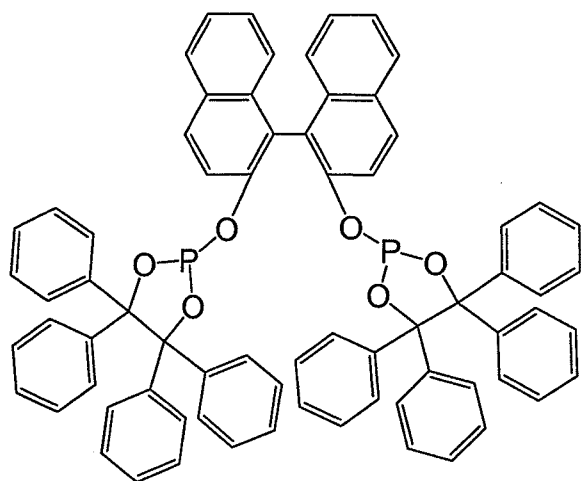
**III**

which may be present in racemic, atropisomerically enriched or atropisomerically pure form.

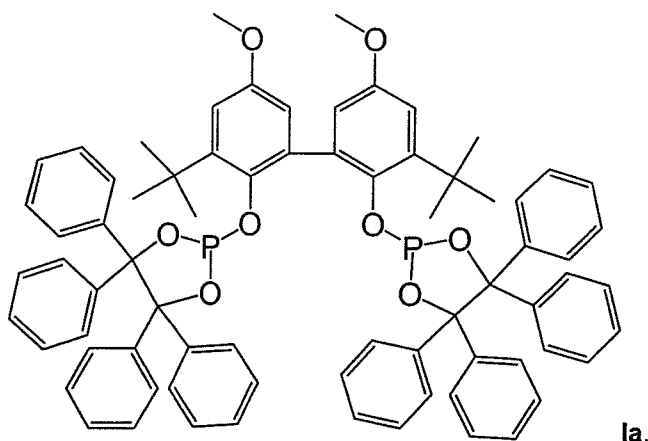
Particularly preferred inventive bisphosphites are the bisphosphites of the following

10 formulae **Ia** to **Ic**, where **Ic** may be prepared and used as the racemate or in

atropisomerically enriched or atropisomerically pure form.

**Ia****Ib****Ic**

Very particular preference is given to using the catalyst system consisting of rhodium
10 and the bisphosphite with the following structural formula Ia



In the catalyst system, the molar ratio of bisphosphite to rhodium is in the range from less than 100 : 1 to 1 : 1, especially in the range from 90 : 1 to 2 : 1, very particularly
 5 in the range from 10 : 1 to 2 : 1.

The rhodium can be used in the form of salts or complexes, for example in the form of rhodium carbonyls, rhodium nitrate, rhodium chloride, $\text{Rh}(\text{CO})_2(\text{acac})$ (acac = acetylacetonate), rhodium acetate or rhodium carboxylates or rhodium octanoate.

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Bisphosphite ligands and the rhodium compound form, under reaction conditions, the active catalyst species for the homogeneous catalysis. In the course of hydroformylation, on contact of the inventive bisphosphite ligand and of the catalyst metal with synthesis gas, a carbonyl hydride phosphite complex is presumed to be
 15 formed as the active catalyst species. The bisphosphites and any further ligands may be added to the reaction mixture in free form together with the catalyst metal (as a salt or complex), in order to generate the active catalyst species in situ. It is additionally also possible to use an inventive phosphite metal complex which contains the abovementioned bisphosphite ligands and the rhodium metal as a
 20 precursor for the actually catalytically active complex. These phosphite-metal complexes are prepared by reacting rhodium in the form of a chemical compound or in the 0 oxidation state with the inventive bisphosphite ligand.

Fresh bisphosphite can be added to the reaction at any time, in order, for example, to
 25 keep the concentration of free ligand constant.

The concentration of the rhodium in the hydroformylation mixture is preferably 1 ppm by mass to 1000 ppm by mass and preferably 5 ppm by mass to 300 ppm by mass, based on the total weight of the reaction mixture.

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The hydroformylation reactions performed with the corresponding rhodium complexes can be performed by known methods, as described, for example, in J. FALBE, "New Syntheses with Carbon Monoxide", Springer Verlag, Berlin, Heidelberg, New York, page 95 ff., (1980). In these methods, 1-butene is reacted in
10 the presence of the catalyst with a mixture of CO and H₂ (synthesis gas) to give C₅ aldehydes.

In this case, the C₅ aldehyde fraction contains a proportion of greater than 90% by mass, especially of one of greater than 93% by mass, of n-valeraldehyde, more
15 preferably of greater than 95% by mass and most preferably of greater than 98% by mass of n-valeraldehyde.

The hydroformylation is performed at temperatures of 40 to 120°C, preferably at 40 to 110°C, more preferably at 60 to 95°C, most preferably at 70 to 95°C. The pressure
20 is 0.1 to 30 MPa, especially 1 MPa to 6.4 MPa. The molar ratio between hydrogen and carbon monoxide (H₂/CO) in the synthesis gas is preferably 10/1 to 1/10 and more preferably 1/1 to 2/1.

The catalyst system is preferably dissolved homogeneously in the liquid
25 hydroformylation mixture consisting of reactants (olefins and dissolved synthesis gas) and products (aldehydes, alcohols, by-products formed in the process, especially high boilers). Optionally, it is additionally possible to use solvents and/or stabilizer compounds, for example sterically hindered secondary amines or promoters.

30 The process can be performed batchwise or preferably continuously. In a continuous process, it is appropriate, in order to achieve virtually complete 1-butene conversion, to perform the reaction in a plurality of reactors. For example, it is possible to connect

a plurality of stirred reactors and/or bubble column reactors in series. In this case, the liquid and/or gaseous effluent of a reactor can be passed into the next. It is also possible to draw off unconverted feed hydrocarbons from a reactor together with products and excess synthesis gas, to condense out the C₅ products, and to
5 introduce the residual gas into the next reactor. The reaction can also be carried out in a pipe coil with intermediate gas feeding. In addition, the reactor can be carried out in a combination of the reactor types mentioned.

If the aim is not the maximum yield of C₅ aldehydes but a high space-time yield, the
10 hydroformylation can be conducted at least partly at temperatures of more than 100°C. At these temperatures, partial isomerization of 1-butene to the two 2-butenes occurs during the hydroformylation. For example, it would be possible to operate the first reactor or the first reactors in a reactor cascade at temperatures of more than 100°C and the downstream reactor(s) at temperatures of less than 100°C, for
15 example 90°C.

The hydroformylation product can be separated by distillation into at least three fractions, specifically into the isobutene fraction, product fraction (principally C₅ aldehydes) and a high boiler fraction comprising the dissolved catalyst system and
20 one or two further fraction(s) which comprise(s) other unconverted substances from the reactant.

For example, the reaction mixture of the last reactor, after removal of the excess synthesis gas, which can be recycled or discharged completely or partially after
25 condensing out substances present therein, can be separated by a first distillation into a C₄ hydrocarbon mixture and a mixture of C₅ products, high boilers and catalyst system. The two mixtures are separated in further distillation steps.

Another possibility is to remove fractions one by one from the reaction mixture,
30 beginning with the lowest-boiling substance or substance mixtures, until only the high boilers comprising the dissolved catalyst system remain.

Optionally the distillative removal can be preceded by removal of a portion of the catalyst by nanofiltration, as described, for example, in DE 10 2005 046250.

If, for example, the reactant used was a C₄ hydrocarbon mixture which comprised

5 isobutane, n-butane, 1-butene, the two 2-butenes and isobutene, the following fractions are obtained:

a) isobutane (boiling point -11.7°C)

b) isobutene (b.p. -6.9°C)

10 c) mixture of n-butane (b.p. -0.5°C), E-2-butene (b.p. 0.9°C) and Z-2-butene (b.p. 3.7°C)

d) mixture of C₅ aldehydes with valeraldehyde (b.p. 103°C), 2-methylbutanal (b.p. 92 – 93°C) and 3-methylbutanal (b.p. 92.5°C)

e) high boilers comprising the dissolved catalyst system

15 Isobutene removed by the process according to the invention has a purity of more than 99%. Its content of linear butenes is correspondingly below 1%. It can be utilized for the purposes mentioned in the introduction.

The C₅ aldehyde fraction contains small amounts of alcohols which arise through
20 hydrogenation of the aldehydes. The content of valeraldehyde in this fraction is more than 95% by mass. Pure valeraldehyde can be removed from this mixture.

Valeraldehyde is, among other things, an intermediate for n-pentanol, n-pentanoic acid, n-pentylamines or n-pentyl chloride.

25 Aldol condensation of the C₅ aldehyde fraction and total hydrogenation of the aldol condensate affords a decanol mixture containing more than 90% by mass of 2-propylheptanol, which is a sought-after intermediate for the production of plasticizers, detergents and lubricants. Aldol condensation of the C₅ aldehyde fraction, hydrogenation of the olefinic double bond of the aldol condensate and
30 subsequent oxidation of the aldehydic group can provide a decanoic acid mixture with a high proportion of 2-propylheptanoic acid, which can be used, for example, to produce lubricants or detergents.

The fraction comprising the 2-butenes can be utilized in different ways. One possibility is the preparation of oligomers, among which especially the dimers and trimers constitute valuable intermediates for the production of plasticizers and alcohols. The oligomerization can be carried out using acidic or nickel-containing catalysts. When low-branching products are desired, an oligomerization with a nickel-containing, heterogeneous catalyst system is advantageous. One process of this kind is, for example, the OCTOL process of Evonik Oxeno GmbH.

Another utilization of the 2-butenes consists in hydroformylating them to C₅ aldehydes. The hydroformylation can be carried out with different catalysts, and typically forms a mixture of 2-methylbutanal and n-valeraldehyde. When a high proportion of valeraldehyde in the C₅ aldehyde mixture is desired, the use of other catalysts is appropriate. For example, in documents DE 101 08 474, DE 101 08 475, DE 101 08 476 and DE 102 25 282, a catalyst consisting of rhodium and a diphosphine ligand which has a xanthene skeleton is used for the hydroformylation of 2-butenes. Using this catalyst, the ratio between valeraldehyde and 2-methylbutanal is greater than 85:15. High selectivities of valeraldehyde (greater than 95%) can be obtained in the case of use of a catalyst consisting of rhodium and sterically demanding aromatic bisphosphites, as described, for example, in EP 0 213 639.

The C₅ aldehyde mixture thus obtained can be converted, for example by aldol condensation and subsequent hydrogenation of the aldol condensate, to a decanol mixture. In the case of C₅ aldehyde mixtures in which the proportion of n-valeraldehyde is less than 95%, it is advisable to remove a proportion of the 2-methylbutanal by distillation in order to obtain a high-quality decanol mixture with a content of 2-propylheptanol of more than 90%.

The 2-methylbutanal removed can be used for various purposes, for example for preparing isoprene.

When the preparation of decanol from a C₄ hydrocarbon mixture is the aim, it is

appropriate to aldolize the C₅ aldehyde mixtures of the two hydroformylations together.

Examples

5

The hydroformylation test was carried out in a Parr 100 ml autoclave with means of keeping the pressure constant, gas flow meter and paddle stirrer. The autoclave was filled under an argon atmosphere with all compounds specified below, but not yet with the olefin mixture to be hydroformylated. After exchanging the argon atmosphere
10 by purging with synthesis gas (1 : 1 CO/H₂), the reaction mixture was heated with stirring (1000 rpm) and under synthesis gas pressure to the temperature specified in each case, and then the exact target pressure of 20 bar was established.

Subsequently, the olefin mixture to be hydroformylated was added. The synthesis gas pressure was kept constant by means of a pressure regulator over the entire
15 reaction time. The reaction time of the hydroformylation tests was in each case 720 min, intermediate samples having been taken from the autoclave for GC analysis. Subsequently, the reaction mixture was cooled to room temperature, and the autoclave was decompressed and purged with argon.

20 All tests contained 6 g of the olefin mixture to be hydroformylated (raffinate I of the composition specified below), 50 g of eutectic mixture of biphenyl and biphenyl ether (Diphyl®, from Lanxess) and bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (from Ciba) in a molar ratio of 1 : 1 relative to the ligand **1a** used. The precatalyst used was (acetylacetonato)dicarbonylrhodium (from Umicore).

25 Tests were carried out at 90°C, 100°C, 110°C and 120°C. The ratio of ligand **1a** to rhodium was in all cases 5 : 1, the rhodium concentration was 40 ppm and the synthesis gas pressure was 2 MPa.

The analysis was carried out by means of gas chromatography.

30 The raffinate I had in each case the start composition specified in Table 1 (all values in % by mass):

Table 1

Component	Iso-butane	n-Butane	E-2-Butene	1-Butene	Iso-butene	Z-2-Butene	1,3-Butadiene	Remainder
in % by mass	4.09	10.63	7.69	26.81	45.72	4.68	0.18	0.20

Example: Hydroformylation of raffinate I at different temperatures

- 5 The hydroformylation of raffinate I of the above composition was carried out at 90°C, 100°C, 110°C and 120°C. In all cases, no 1-butene could be detected any longer after 720 minutes, which showed quantitative conversion of the 1-butene. At the same time, the particular isobutene conversion (formation of 3-methylbutanal) after 720 minutes was at the following values:

- 10 90°C: 0.58%
 100°C: 0.67%
 110°C: 0.80%
 120°C: 1.17%

- 15 The hydrogenation to saturated species likewise played only a minor role and was less than one per cent, and less than one-and-a-half per cent at temperatures from 110°C.

- In the tests at 110°C and 120°C, there was also a certain degree of isomerising
 20 hydroformylation of the 2-butenes toward the end of the reaction, such that the yield of n-valeraldehyde in these cases after 720 minutes was 102% and 105% respectively, based on 1-butene used in the raffinate I.

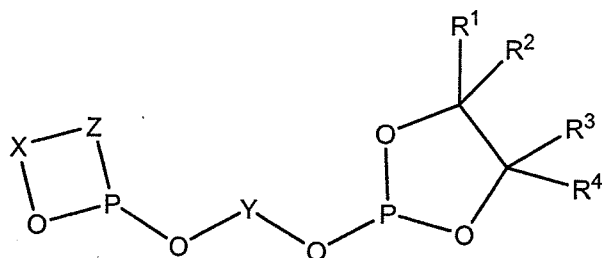
- The pentanal formed from 1-butene (and, from 110°C, to a minor degree from
 25 2-butenes) after 720 minutes was obtained with the following linearities:

- 90°C: 99.1%
 100°C: 99.0%
 110°C: 98.9%
 120°C: 98.4%

The differences from 100% are 2-methylbutanal.

Claims

1. Process for removing 1-butene from C₄-containing hydrocarbon mixtures comprising isobutene and 1-butene by hydroformylation, the catalyst system used consisting of one or the transition metals of groups 8 to 10, preferably rhodium, and a bisphosphite ligand of the following formula I



where X = divalent

substituted or unsubstituted bisalkylene or bisarylene radical which contains one or more heteroatom(s), Y = divalent substituted or unsubstituted bisarylene or bisalkylene radical which contains one or more heteroatom(s), Z = oxygen or NR⁹, and R¹, R², R³, R⁴ are identical or different, substituted or unsubstituted, connected, unconnected or fused aryl or heteroaryl radicals, and R⁹ = hydrogen or substituted or unsubstituted alkyl or aryl radical which contains one or more heteroatom(s), the bisphosphite ligand of the above-specified formula I being used in an excess of a molar ratio of 100 : 1 to 1 : 1 relative to the transition metal, and less than 5% of the isobutene present being converted at a 1-butene conversion of more than 95%.

2. Process according to claim 1, characterized in that the concentration of the transition metal in the hydroformylation mixture is 1 ppm by mass up to 1000 ppm by mass based on the total weight of the reaction mixture.
3. Process according to either of claims 1 and 2, characterized in that the molar ratio of bisphosphite to rhodium is in the range from 90 : 1 to 1 : 1.
4. Process according to any one of claims 1 to 3, characterized in that the molar ratio of bisphosphite to rhodium is in the range from 10 : 1 to 2 : 1.

5. Process according to any one of claims 1 to 4, characterized in that less than 5% of the isobutene present is converted at a 1-butene conversion of more than 99%.
- 5 6. Process according to any one of claims 1 to 5, characterized in that 1-butene is hydroformylated with an n-/iso selectivity of more than 97%.
7. Process according to any one of claims 1 to 6, characterized in that 1-butene in the feed hydrocarbon mixture is removed to an extent of more than 99% from C₄-
10 containing hydrocarbon mixtures by hydroformylation at temperatures of 40 to 120°C.
8. Process according to any one of claims 1 to 7, characterized in that 1-butene in the feed hydrocarbon mixture is removed to an extent of more than 99% from C₄-
15 containing hydrocarbon mixtures by hydroformylation at temperatures of 70 to 95°C.
9. Process according to any one of claims 1 to 8, characterized in that the hydroformylation is carried out within a pressure range from 0.5 to 30 MPa.
20
10. Process according to any one of claims 1 to 9, characterized in that the hydroformylation is carried out within a pressure range from 1.0 to 6.4 MPa.
11. Process according to any one of claims 1 to 10, characterized in that the process
25 is performed continuously.
12. Process according to any one of claims 1 to 11, characterized in that the C₄-containing hydrocarbon mixture comprises 2-butenes.
- 30 13. Process according to any one of claims 1 to 12, characterized in that the reaction mixture is separated into C₅ aldehydes, isobutene, a high boiler fraction comprising the dissolved catalyst system and further C₄ hydrocarbons.

14. Process according to claim 13, characterized in that the further C₄ hydrocarbons are subjected to an isomerizing hydroformylation to give valeraldehyde.
- 5 15. Process according to claim 14, characterized in that the C₅ aldehydes obtained from selective hydroformylation and isomerizing hydroformylation are combined.
16. Process according to claim 13 or 15, characterized in that the C₅ aldehydes removed are subjected to an aldol condensation, dehydration and subsequent
10 hydrogenation to 2-propylheptanol.