

Preparation of n-butyl alkyl ethers

- 5 The present invention relates to a process for preparing n-butyl alkyl ethers by reacting butadiene with alcohols to give a mixture of 1- and 3-alkoxybutene, isomerizing the 3-alkoxybutene to give 1-alkoxybutene and hydrogenating the 1-alkoxybutene.
- 10 n-Butyl alkyl ethers are products of the chemical industry and have a variety of uses. Thus, for example, di-n-butyl ether is used as solvent for various natural and synthetic resins, fats, oils and Grignard reactions. Di-n-butyl ether mixed with ethanol or butanol is also employed for dissolving ethylcellulose.
- 15 Industrially, di-n-butyl ether is produced virtually exclusively by the dehydration of n-butanol by various processes in which the reaction is carried out, for example, in the presence of sulfuric acid or catalysts such as iron chloride, copper sulfate, silica gel or aluminum oxide (Kirk-Othmer: Encyclopedia of Chemical Technology, 4th Edition, Volume 9, pp. 860 - 876, John Wiley & Sons, New York 1992; Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Volume A 10, pp. 23 - 34, Verlag Chemie Weinheim). These processes, in particular the dehydration with
- 20 the aid of heterogeneous catalysts, require high reaction temperatures which lead to secondary reactions. Furthermore, only alcohols having a short chain length (C_1-C_3) can be successfully dehydrated in the homogeneous processes using sulfuric acid or metal salts.
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- 30 Unsymmetrical n-butyl alkyl ethers, for example 2-(n-butoxy)ethanol or 1-(n-butoxy)propan-2-ol, which serve as solvents in the surface coatings industry, are customarily prepared by reacting n-butanol with ethylene oxide or propylene
- 35 oxide (Encyclopedia of Chemical Processing and Design, Volume 20, pp. 258-274, Marcel Dekker, Inc, New York and Basel 1984). It is known from US 4 843 180, for example, that dienes react with hydroxy compounds to give unsaturated butyl ethers which can be hydrogenated in a further stage to give mixtures of linear and
- 40 predominantly branched saturated ethers.

The present invention therefore seeks to propose a process for preparing n-butyl alkyl ethers starting from the readily

45 available butadiene. Although 1,3-butadiene is available in large amounts and is a very inexpensive raw material, no industrially useable process for preparing n-butyl alkyl ethers from 1,3-butadiene or butadiene-containing hydrocarbon mixtures has

hitherto been known. Reasons for this are both the tendency of 1,3-butadiene to undergo dimerization and polymerization reactions and the formation of mixtures of 1,2- and 1,4-adducts in addition reactions. The cause of this chemical behavior is the presence of two conjugated double bonds in the 1,3-butadiene molecule ((Kirk-Othmer: Encyclopedia of Chemical Technology, 4th Edition, Volume 4, pp. 676-683, John Wiley & Sons, New York 1992).

Thus, the reaction of butadiene with alcohols and also the hydrogenation of the butenyl ethers have been described in numerous publications without an industrially useable process having been found up to the present time.

In particular, WO 95/19334 discloses and describes in detail the addition of alcohols onto butadiene to give the alkyl butenyl ethers and the isomerization of the 3-alkoxybut-1-ene compound. However, a further isomerization to give the enol ether takes place in that publication. A hydrogenation of the 1-alkoxybut-2-enes is not considered and described.

Only a few examples are known for the hydrogenation of general allyl ethers to give n-butyl alkyl ethers. US 3 769 352, US 3 670 029 and US 4 843 180 merely mention that the unsaturated ethers can be hydrogenated.

It is an object of the present invention to find an industrially useable, economical process for preparing n-butyl alkyl ethers which makes it possible to prepare these products in high yield and with high selectivity.

We have found that this object is achieved by a process for preparing n-butyl alkyl ethers which comprises

a) reacting 1,3-butadiene or a butadiene-containing hydrocarbon mixture with an alcohol of the formula I

ROH I,

where the radical R is a C₂-C₂₀-alkyl, alkenyl, cycloalkyl or cycloalkenyl group, each of which may be unsubstituted or substituted by 1 or 2 C₁-C₁₀-alkoxy or hydroxy groups, a C₆-C₁₀-aryl group or a C₇-C₁₁-aralkyl group or the methyl group, at elevated temperature and elevated pressure in the presence of a Brönsted acid or in the presence of a complex

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of an element from group Ib, VIIb or VIIIb of the Periodic Table of the Elements with phosphorus- or nitrogen-containing ligands to give a mixture of adducts of the formulae II

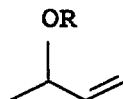
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II

and III

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III ,

where R is as defined above,

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- b) separating the adducts of the formula II and III,
- c) isomerizing the adduct III in the presence of a catalyst as indicated for (a) to give the adduct II and
- d) hydrogenating the adduct II in the liquid phase in the presence of a homogeneous or heterogeneous transition metal catalyst or in the gas phase in the presence of a heterogeneous transition metal-containing catalyst to give an

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n-butyl alkyl ether of the formula IV



IV.

The process of the present invention thus comprises 4 stages, where the subreactions (a) and (c) can be carried out, as a matter of choice, individually and in succession or in parallel or in one process stage. In the latter case, the isomerization of the adduct III to form the adduct II according to subreaction c) after return of the adduct III to the process stage in which the alcohol ROH is added onto 1,3-butadiene proceeds simultaneously with the addition according to subreaction (a).

In general, the catalyst used in one plant unit for the subreaction (a) is able, under the reaction conditions employed there, to catalyze both the isomerization of the adduct III to give the adduct II and the addition of the alcohol I onto 1,3-butadiene, so that there is no strict spatial separation of these subreactions. A plant unit for stage (a) can comprise either a single reactor or a plurality of reactors connected in series which are charged with the same catalyst or, if desired, with different catalysts and are operated in the same operating mode and under identical or different temperature and pressure

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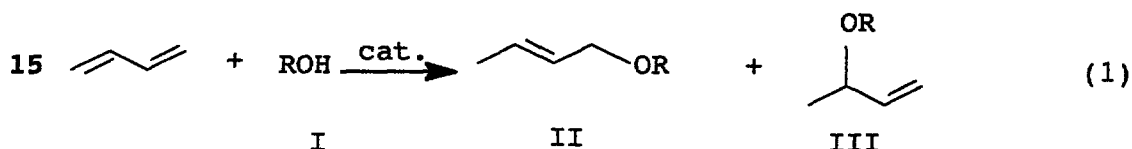
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conditions. In the present context, operating mode is in each case operation in the liquid phase using a homogeneous catalyst or a heterogeneous catalyst or, in exceptional cases, operation in the gas phase.

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The process of the present invention is explained in more detail below:

- 10 In stage (a), 1,3-butadiene or a butadiene-containing hydrocarbon mixture is reacted with the alcohol ROH I according to equation (1)



- 20 in the presence of a catalyst to give the 1,4 adduct of the formula II and the 1,2-adduct of the formula III. In the 1,4-adduct II formed, the double bond can be in either the cis or trans configuration, but this is not important for the further course of the process. The adducts II and III are generally
- 25 formed in a molar ratio of from 1:1 to 1:3, depending on the reaction conditions and catalyst employed.

- The type of alcohol ROH I used in the reaction is generally not critical for the process. It is possible to use either primary or
- 30 secondary alcohols, but preference is given to using primary alcohols. It is possible to use either aliphatic, cycloaliphatic, aromatic or araliphatic alcohols, with preference being given to using aliphatic and araliphatic alcohols. In general, alcohols ROH I used in the process of the present invention are ones in
- 35 which the radical R is a C₁-C₂₀-alkyl group, a C₂-C₁₀-alkenyl group, e.g. the 2-butenyl group, preferably a C₁-C₄-alkyl group, in particular the n-butyl group, a C₆-C₁₀-aryl group, preferably the phenyl group, or a C₇-C₁₁-aralkyl group, preferably the benzyl group. The radicals R may be unsubstituted or substituted by
- 40 substituents such as C₁-C₁₀-alkoxy and/or hydroxyl groups. Alcohols ROH I which can be used thus also include diols, preferably ethylene glycol or 1,2-propanediol, or triols or alkoxyalcohols. Of course, alcohols having a higher number of carbon atoms can also be used. Since such higher alcohols are
- 45 generally more expensive than lower alcohols, the use of lower

alcohols is preferred for economic reasons. Among the alcohols mentioned, n-butanol for preparing di-n-butyl ether is preferred.

Many catalysts can be used in stage (a), for example Brönsted acids or complexes of transition metals from groups Ib, VIIB and VIIIB of the Periodic Table of the Elements, in particular of palladium and nickel.

Suitable Brönsted acids are, for example, conventional, non-oxidizing Brönsted acids such as hydrohalic acids, e.g. hydrochloric acid, sulfuric acid, phosphoric acid, perchloric acid, hydrofluoric acid, tetrafluoroboric acid, methanesulfonic acid or toluenesulfonic acid, but preferably solid Brönsted acids, in particular organic or inorganic cation exchangers.

The complexes, in particular phosphine complexes, of the transition metal catalysts comprising an element from group Ib, VIIB and VIIIB of the Periodic Table of the Elements, for example, copper, nickel, rhodium, palladium, platinum, rhenium or iridium, preferably palladium or nickel, can be homogeneously dissolved in the reaction medium or be present in heterogeneous form.

The alkyl butenyl ethers are generally prepared according to the disclosures of WO 95/19334 in respect of both the catalysts used and the process conditions, so that this reference and the previous literature cited therein are expressly incorporated by reference in the present application.

The molar ratio of alcohol/1,3-butadiene can be selected within a wide range. In general, a molar ratio of alcohol ROH/1,3-butadiene of from 0.5:1 to 10:1, preferably from 1:1 to 3.0:1 and particularly preferably from 1.5:1 to 2.5:1, is employed. The alcohol ROH is advantageously always employed in an at least one molar excess since a higher yield can be achieved thereby. The reaction of the alcohol ROH I with 1,3-butadiene is generally carried out at from 20 to 150°C, preferably from 50 to 120°C, in particular from 60 to 110°C, and at a pressure of generally from 1 to 100 bar, preferably from 5 to 50 bar, in particular from 10 to 30 bar, when the process is carried out in the liquid phase. The pressure is advantageously selected such that the 1,3-butadiene or the butadiene-containing hydrocarbon mixture is liquid at the reaction temperature employed. The use of a higher pressure is possible. The reaction temperature

employed is advantageously optimized in respect of the particular catalyst used in a preliminary experiment.

5 In general, the alcohol ROH/1,3-butadiene mixture is passed through the fixed catalyst bed at a space velocity of from 0.01 to 0.5 g/cm³·h, preferably from 0.05 to 0.4 g/cm³·h and particularly preferably from 0.10 to 0.25 g/cm³·h. The addition of a solvent to the reaction mixture is possible, but generally not necessary since the alcohol used as well as the adducts II and 10 III can also function as solvent. The residence time of the alcohol ROH/1,3-butadiene mixture in the reactor is generally from 1 to 6 hours and, as a rule, is dependent on the reaction temperature employed.

15 If the addition of the alcohol ROH I onto 1,3-butadiene or the butadiene-containing hydrocarbon mixture is carried out in the gas phase, it is usual to employ temperatures of less than 120°C and a pressure of generally less than 20 bar. If desired, the reaction gas can be mixed with a gas which is inert under the 20 reaction conditions, e.g. nitrogen, but the reaction gas is generally used undiluted.

In place of pure 1,3-butadiene, it is also possible to use 25 1,3-butadiene-containing hydrocarbon mixtures as raw material. Such hydrocarbon mixtures are formed, for example, as C₄ fraction in steam crackers. Before they are used, these hydrocarbon mixtures are advantageously freed of any acetylenic or allenic hydrocarbons present therein by partial hydrogenation of the 30 latter (Weissermel, Arpe: Industrielle Organische Chemie; 3rd Edition, VCH Verlagsgesellschaft, Weinheim 1988) and, if desired, freed of isobutene. The 1,3-butadiene-containing hydrocarbon mixtures can then be introduced into the subreaction (a) in a similar manner to pure 1,3-butadiene. The saturated or 35 monoolefinic hydrocarbons present in these hydrocarbon mixtures which have not reacted in subreaction (a) are advantageously removed from the reaction product, for example by means of a gas/liquid separator or a pressure distillation. The adducts of the formulae II and III obtained in the reaction of these 40 hydrocarbon mixtures in subreaction (a) can be further processed to give the n-butyl alkyl ethers in the same way as the adducts II and III produced in subreaction (a) when using pure 1,3-butadiene.

45 The reaction product from subreaction (a) of the process of the present invention generally comprises, apart from unreacted 1,3-butadiene or olefinic hydrocarbons, the adducts of the

formulae II and III as well as possibly, particularly when using Brönsted acids as catalysts, a plurality of isomers of the respective alkoxyoctadiene, which will hereinafter be referred to by the collective term alkoxyoctadiene. The alkoxyoctadiene is
5 formed in the addition of the alcohol ROH I onto 1,3-butadiene in a secondary reaction in which 1,3-butadiene first dimerizes to give octatriene onto which the alcohol ROH I subsequently adds to form the alkoxyoctadiene. Apart from these constituents, the reaction product from subreaction (a) can also contain small
10 amounts of other by-products, for example octatriene, vinylcyclohexene, alkoxydodecatrienes, formed by trimerization of the 1,3-butadiene to form dodecatetraene and subsequent addition of the alcohol ROH, also dodecatetraene and dialkoxybutane. The formation of these by-products can be influenced and if desired
15 minimized by the way in which the subreaction (a) is carried out, for example by the choice of the 1,3-butadiene/alcohol ROH ratio, ie. an excess of butanol, in the reaction mixture, the choice of the reaction temperature and the pressure.

20 The adduct of the formula II required for preparing n-butyl alkyl ethers is separated from its isomer 3-alkoxybut-1-ene of the formula III, which is present in the reaction product in approximately the same amount, in the distillation stage (b) and the undesired isomer 3-alkoxybut-1-ene III is converted into the
25 desired 1-alkoxybut-2-ene II.

The separation of adduct III can be advantageously performed by fractioning the reaction product from subreaction (a), by
30 fractional distillation after prior removal of unreacted 1,3-butadiene, for example in a gas/liquid separator or a pressure distillation.

In this fractional distillation, the by-products present in the
35 reaction product from subreaction (a), viz. 1,3-butadiene dimers and trimers and also their adducts with the alcohol ROH I and possibly multiply alkoxyated by-products, as well as excess alcohol ROH I can also be separated from the adduct II. Since these by-products generally do not interfere during the further
40 course of the process, they can be left in the product at this stage and recovered only in the distillation of the alkyl butyl ether. The distillation can also be carried out so as to separate off, apart from the adduct III, only some of the by-products, in particular the olefinic 1,3-butadiene dimers and trimers and also
45 multiply alkoxyated by-products, while other by-products, in particular the alkoxyoctadiene and if desired the alkoxydodecatriene, are processed further together with the

adduct II in the subsequent subreactions, with these by-products from subreaction (a) forming octyl or dodecyl alkyl ethers as end products.

5 According to the preferred embodiment of the process of the present invention, the adduct III separated from the desired adduct as well as the unreacted 1,3-butadiene are returned to the subreaction (a) where the isomerization of the adduct III to give the adduct II takes place simultaneously with the addition
10 reaction or the returned material leads to the suppression of the new formation of the undesired adduct III, so that when using this circular mode of operation virtually only the desired adduct II, but not its undesired isomer III, is formed in the total balance.

15 Instead of being returned to the subreaction (a), the adduct III can also be isomerized in a separate isomerization stage (c) by passing the adduct III separated from the adduct II through, for example, a reactor charged with an isomerization catalyst, in
20 general a catalyst as used in stage (a), fractionating the product from this reactor, which comprises the isomerization mixture of adduct III and adduct II formed therein, into adduct II and adduct III, for example by distillation, further
25 processing the newly formed adduct II to give the n-butyl alkyl ether and returning the adduct III to the isomerization reactor.

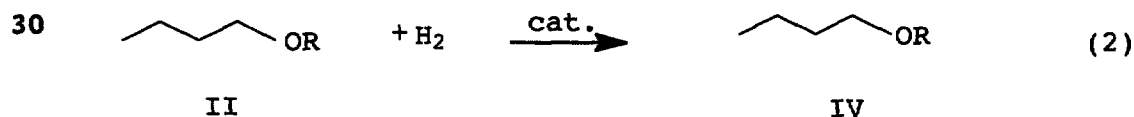
The isomerization of the adduct III into the adduct II can be carried out in the presence or absence of a solvent; preference
30 is given to working without solvent. If the isomerization is carried out in the presence of a solvent, use is generally made of high-boiling solvents such as ethers, for example diethylene or triethylene glycol dimethyl ether, diethylene or triethylene glycol dibutyl ether, sulfoxides, such as dimethyl sulfoxide or
35 sulfones such as sulfolane, high-boiling aromatic or aliphatic hydrocarbons or halogenated aliphatic or aromatic solvents, e.g. dichlorobenzene. The use of low-boiling solvents is likewise possible but generally requires an increased outlay in the distillative separation of the product from the isomerization
40 reactor into the adducts II and III.

The isomerization of the 3-alkoxybut-1-enes into the 1-alkoxybut-2-enes is also carried out generally according to the disclosures of WO 95/19334, so that, in respect of the catalysts
45 and the process procedure, this document is expressly incorporated by reference into the present application.

According to a preferred embodiment, the addition of stage (a) and the isomerization (c) are carried out in the presence of up to 20 % by weight, e.g. from 0.0001 to 20 % by weight, preferably from 0.001 to 10 % by weight and in particular from 0.01 to 5 % by weight, of water.

This measure increases the yield of the desired alkyl butenyl ethers.

- 10 The water can be introduced by addition to any of the stages (a) to (c) or by omitting the removal of water from the ion exchanger, as is otherwise customary. In the separation of the isomers II and III by distillation, azeotropes of ether, alcohol and water are generally formed so that return of the azeotrope comprising the 3-alkylbutenyl ether ensures a certain water content in stage 1. This water content is generally sufficient. If desired, the water content can be increased further by addition of more water. The optimum water content is advantageously determined, depending on the type of catalyst, by a preliminary experiment. For example, when using PUROLITE® CT 175 (from Purolite, Deutschland GmbH Ratingen) it is from 0.5 to 2 % by weight.
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- 25 In a fourth stage (d), the adduct II is catalytically hydrogenated using catalysts known per se to give the ether of the formula IV.



- 35 The hydrogenation of the adduct III to form the n-butyl alkyl ether IV can be carried out in the liquid phase or preferably in the gas phase. When carrying out the reaction step in the liquid phase, it is possible to employ either homogeneous or heterogeneous catalysts. If it is carried out in the gas phase, heterogeneous catalysts are generally preferred.
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As homogeneous catalysts for hydrogenating the adduct II to give the n-butyl alkyl ether IV, it is possible to use many transition metal compounds, in particular those which comprise elements from transition groups V, VI, VII and VIII of the Periodic Table of

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the Elements, preferably iron, cobalt, nickel, ruthenium, rhodium, palladium, platinum, osmium and/or iridium.

Suitable catalysts are, for example, the salts of these transition metals, in particular their halides, nitrates, sulfates, phosphates and carboxylates soluble in the reaction medium, for example their C₁-C₂₀-carboxylates, such as formates, acetates, trichloroacetates, propionates, 2-ethylhexanoates, decanoates, also the citrates, tartrates, malates, malonates, maleinates or fumarates, sulfonates, such as methanesulfonates, benzenesulfonates, naphthalenesulfonates, toluenesulfonates or trifluoromethanesulfonates, cyanides, tetrafluoroborates, perchlorates or hexafluorophosphates, also soluble salts of the oxo acids of these metals, in particular the alkali metal, alkaline earth metal or onium salts such as ammonium, phosphonium, arsonium or stibonium salts, soluble inorganic complexes of these elements, in particular their aquo, halo, phosphine, phosphite, cyano or amino complexes as well as the complexes of these transition metals with chelating agents such as acetylacetone, dioximenes, e.g. diacetyl dioxime, furil dioxime or benzil dioxime, ethylenediaminetetraacetic acid, nitrilotriacetic acid, nitrilotriethanol, ureas or thioureas, diphosphines, diphosphites, bipyridines, terpyridines, phenanthrolines, 8-hydroxyquinoline, crown ethers or polyalkylene glycols, and also organometallic compounds of these transition metals, for example carbonyl complexes such as HRuCl(CO)(PPh₃)₃, HRuCl(CO)(hexyldiphenylphosphine)₃, RuH₂(CO)(PPh₃)₃, RuH(CO)(CH₃CO₂)(PPh₃)₂, RuH₂(PPh₃)₃, HRh(CO)(PPh₃)₃ or IrCl(CO)(PPh₃ = triphenylphosphine).

Preferred salt-like homogeneous catalysts are the halides, in particular the chlorides, nitrates, sulfates, sulfonates, carboxylates and cyanides of rhodium, ruthenium, palladium, platinum and iridium.

Preferred homogeneous catalysts for carrying out the hydrogenation (d) are complexes of the transition metals mentioned, in particular of cobalt, nickel, rhodium, ruthenium, palladium, platinum and iridium, having monodentate or multidentate, in particular bidentate, phosphine or phosphite ligands and/or nitrogen-containing ligands in which the complex-forming properties are derived from the (-N=C-C=N-) structural unit, for example 2,2'-bipyridine or 1,10-phenanthroline, and also the ligands derived from these base structures by substitution or fusion.

Organometallic transition metal compounds which are preferably used as homogeneous catalysts for carrying out the subreaction (d) are, for example, carbonyl complexes such as $\text{HRh}(\text{PPh}_3)_3(\text{CO})$, $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$, $\text{RuH}(\text{CO})(\text{CH}_3\text{CO}_2)(\text{PPh}_3)_2$, $\text{RuH}(\text{CO})(\text{C}_9\text{H}_{19}\text{CO}_2)(\text{PPh}_3)_2$ or $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_3$.

- Suitable phosphine ligands are, for example, the same phosphine ligands mentioned for carrying out the subreaction (a), to which reference is hereby made. Suitable 2,2'-bipyridine or 1,10-phenanthroline ligands are, for example, the ligands mentioned for carrying out the subreaction (a) and also their derivatives and structural analogs mentioned there, to which reference is hereby made.
- Suitable phosphite ligands are, for example, trialkyl phosphites, alkyl diaryl phosphites, triaryl phosphites, alkyl diphosphites, aryl diphosphites, alkyl aryl diphosphites. The alkyl-bearing phosphite ligands can contain identical or different $\text{C}_1\text{-C}_{10}$ -, preferably $\text{C}_1\text{-C}_6$ -alkyl or cycloalkyl groups. The aryl-bearing phosphite ligands can contain identical or different $\text{C}_6\text{-C}_{12}$ -aryl groups, in particular the phenyl or naphthyl group but also the biphenyl group. Furthermore, the transition metals can be complexed using phosphite ligands bearing heterocycloaliphatic groups such as pyrrolidine, imidazolidine, piperidine, morpholine, oxazolidine, piperazine or triazolidine groups or heteroaromatic groups such as pyrrol, imidazole, oxazole, indole, pyridine, quinoline, pyrimidine, pyrazole, pyrazine, pyridazine or quinoxaline groups together with other alkyl or aryl groups. The alkyl or aryl groups of the phosphite ligands can be unsubstituted or bear substituents which are inert under the reaction conditions, for example $\text{C}_1\text{-C}_4$ -alkoxy, di- $\text{C}_1\text{-C}_4$ -alkylamino, $\text{C}_1\text{-C}_6$ -alkyl or hydroxy, nitro, cyano or sulfonate groups. The sulfonate-substituted phosphite ligands and their complexes are generally soluble in water. Suitable phosphite ligands are, for example, trimethyl phosphite, triethyl phosphite, tripropyl phosphite, triisopropyl phosphite, tributyl phosphite, tricyclopentyl phosphite, tricyclohexyl phosphite, triphenyl phosphite and also the monophosphite and diphosphite ligands described in EP-A 472 071, EP-A 213 639, EP-A 214 622, DE-A 27 33 796, EP-A 2 261, EP-A 2 821, EP-A 9 115, EP-A 155 508, EP-A 353 770, US-A 4 318 845, US-A 4 204 997 and US-A 4 362 830.

In the hydrogenation (d) using phosphine or phosphite complexes homogeneously soluble in the reaction medium as catalysts, it can prove to be advantageous to additionally add a phosphine or phosphite, preferably the phosphine or phosphite serving as

ligand in the homogeneous catalyst used, and/or an acid such as an alkanolic acid, e.g. acetic acid, ethylhexanoic acid or decanoic acid, or toluenesulfonic acid or a phenol to the reaction mixture. Such an addition can prolong the life of the homogeneous catalyst and, furthermore, improve the selectivity of the reaction of the adduct II to form the n-butyl alkyl ether IV and thus improve the selectivity of the overall process. A similar advantageous effect can be achieved by the addition of carbon monoxide to the reaction mixture, particularly when using carbonyl-containing transition metal complexes as homogeneous catalysts.

To achieve the abovementioned effects, the phosphine or phosphite is generally added in a molar amount which is from 1 to 100 times, preferably from 1 to 20 times and particularly preferably from 1 to 5 times, the molar amount of the phosphine or phosphite complex of the transition metal. If the transition metal complex serving as homogeneous catalyst is generated in situ in the reaction mixture, an appropriately high excess of phosphine or phosphite ligand, based on the respective transition metal, is advantageously used.

The transition metal catalysts which are homogeneously soluble in the reaction medium are generally used in amounts of preferably from 0.02 to 0.2 mol%, based on the adduct II fed to the reactor. The optimum amount for the homogeneous catalyst used in each case is advantageously determined in a preliminary experiment.

The hydrogenation (d) with the aid of the homogeneous catalysts mentioned can be carried out batchwise, e.g. in stirred reactors, or continuously, e.g. in loop reactors, bubble columns or cascades of stirred reactors, generally at above 60°C and at a pressure of generally from 5 to 100 bar, preferably from 10 to 60 bar. The reaction of the adduct II to give the n-butyl alkyl ether IV can be carried out in the presence or absence of added solvents such as aliphatic or aromatic hydrocarbons, e.g. toluene, benzene, xylene or cyclohexane, alcohols such as butanols, higher fatty alcohols or glycols, ethers such as tetrahydrofuran, dioxane or low molecular weight polyalkylene glycols, halogenated aliphatic or aromatic hydrocarbons such as chloroform, dichloromethane, chlorobenzene or dichlorobenzene, sulfoxides or sulfones such as dimethyl sulfoxide or sulfolane.

If no further solvents are added in the hydrogenation, the reactants themselves, ie. the adduct II and the n-butyl alkyl ether IV, also serve to dissolve the homogeneous catalysts.

- 5 To hydrogenate the adduct II, hydrogen is mixed in in a molar ratio, based on the adduct II fed to the reactor, of generally from 1:1 to 100:1, preferably from 1:1 to 50:1 and particularly preferably from 1:1 to 10:1. When the process is carried out batchwise, this mixing in can be carried out by injecting the
10 necessary amount of hydrogen into the reactor or by dispersing the hydrogen in the reaction medium, for example by means of bubble columns or by means of loop reactors fitted with jet nozzles for dispersing the hydrogen. The mixing in of the hydrogen is generally carried out when charging the reactor with
15 the adduct II and the homogeneous catalyst, but can also advantageously be fed into the reaction apparatus subsequently. Which of these procedures is selected depends on the catalyst used and the pressure and temperature conditions employed in each case as well as on the construction of the reactor. The optimum
20 procedure is advantageously determined in a preliminary experiment. In the case of a continuous hydrogenation, eg. in a tube reactor, a bubble column reactor or a packed column, the hydrogen can be introduced continuously into the reactor in a similar manner together with the other reactants or separately.
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- After the reaction is complete, the reaction product is generally worked up by distillation, where the homogeneous catalyst used can be recovered from the bottoms from the distillation and can
30 be reused if desired. If recycling of the catalyst in the process of the present invention is desired, a further solvent, preferably a solvent which boils at a higher temperature than the n-butyl alkyl ether, can advantageously be added to the reaction mixture. If the homogeneous catalyst used is chemically and
35 thermally stable under the conditions of the distillation, the addition of a high-boiling solvent can be omitted and the homogeneous catalyst can be returned in solid form to the reaction.

- 40 In a further preferred embodiment of the process of the invention, the hydrogenation of the adduct II to give the n-butyl alkyl ether IV is carried out using a heterogeneous catalyst, with the process being carried out either in the liquid phase or preferably in the gas phase.

Among these hydrogenation catalysts, preference is given to those which comprise one or more elements of groups Ib, VIb, VIIb and VIIIb, possibly in combination with one or more elements of group Vb, of the Periodic Table of the Elements, in particular copper, zinc, chromium, molybdenum, tungsten, rhenium, ruthenium, cobalt, nickel, rhodium, iridium, palladium and/or platinum, possibly in combination with iron.

- 10 Particularly active hydrogenation catalysts such as nickel, cobalt or the platinum metals can advantageously be doped with main group elements which act as catalyst poison and in this way be partially poisoned. This measure enables a higher selectivity to be achieved in the hydrogenation to give the n-butyl alkyl ethers. Suitable main group elements are, for example, the
- 15 chalcogens such as sulfur, selenium and tellurium, and also the elements phosphorus, arsenic, antimony, bismuth, tin, lead and thallium.
- 20 As heterogeneous catalysts, it is possible to use, for example, precipitated catalysts. Such catalysts are prepared by precipitating their catalytically active components from corresponding salt solutions, in particular from the solutions of nitrates and/or acetates of the active components, for example by
- 25 addition of solutions of alkali metal and/or alkaline earth metal hydroxide and/or carbonate solutions, as, for example, sparingly soluble hydroxides, hydrated oxides, basic salts or carbonates, subsequently drying the resulting precipitants and then calcining them at generally from 300 to 700°C, in particular from 400 to
- 30 600°C into the relevant oxides, mixed oxides and/or mixed-valence oxides which are reduced to the relevant metals and/or to oxidic compounds of low oxidation state and converted into the actual catalytically active form, for example by treatment with reducing agents such as hydrogen or hydrogen-containing gases at generally
- 35 from 50 to 700°C, in particular at from 100 to 400°C. The reduction is generally continued until water is no longer formed. In the preparation of precipitated catalysts comprising a support material, the precipitation of the catalytically active components can be carried out in the presence of the relevant
- 40 support material. However, the catalytically active components can advantageously also be precipitated simultaneously with the support material from the corresponding salt solutions.

Preference is given to using hydrogenation catalysts which have

45 the hydrogenation-catalyzing metals or metal compounds deposited on a support material. Apart from the abovementioned precipitated catalysts comprising a support material in addition to the

catalytically active components, other supported catalysts suitable for the hydrogenation (d) are generally those in which the catalytically active components have been applied to a support material by, for example, impregnation.

5

The way in which the catalytically active metals are applied to the support is generally not critical and can be achieved in a variety of ways. The catalytically active metals can be applied to these support materials by, for example, impregnation with
10 solutions or suspensions of the salts or oxides of the elements concerned, drying and subsequent reduction of the metal compounds to the relevant metals or compounds of a low oxidation state by means of a reducing agent, preferably by means of hydrogen, hydrogen-containing gases or hydrazine. Another possible way of
15 applying the catalytically active metals to the supports is impregnating the supports with solutions of salts which are readily decomposed thermally, for example nitrates or complexes which are readily decomposed thermally, eg. carbonyl or hydrido complexes of the catalytically active metals and to heat the
20 resulting impregnated support to from 300 to 600°C in order to thermally decompose the adsorbed metal compounds. This thermal decomposition is preferably carried out under a protective gas atmosphere. Suitable protective gases are, for example, nitrogen, carbon dioxide, hydrogen or the noble gases. Furthermore, the
25 catalytically active metals can be deposited on the catalyst support by vapor deposition or by flame spraying.

The content of the catalytically active metal in the supported catalysts is, in principle, not critical for the success of the
30 process of the present invention, with higher contents of catalytically active metals in these supported catalysts naturally leading, as a rule, to higher space-time conversions than in the case of lower contents. However, use is generally
35 made of supported catalysts whose content of catalytically active metals is from 0.1 to 80 % by weight, preferably from 0.5 to 50 % by weight, based on the total catalyst. Of course, it is also possible for a plurality of the catalytically active metals to be applied to the respective support material. Furthermore, the
40 catalytically active metals can be applied to the support by, for example, the methods of DE-A 2519817, EP-A 147219 and EP-A 285420. In the catalysts as described in the abovementioned documents, the catalytically active metals are present as an alloy which is produced by thermal treatment and/or reduction of
45 the salts or complexes of the abovementioned metals deposited, eg. by impregnation, on a support.

The activation of both the precipitated catalysts and the supported catalysts can also be achieved in situ in the reaction mixture by the hydrogen present therein. However, these catalysts are preferably activated before use.

5

The support materials which can be used are, in general, the oxides of aluminum and titanium, zirconium dioxide, silicon dioxide, kieselguhr, silica gel, clays, eg. montmorillonites, silicates, such as magnesium or aluminum silicates, zeolites, 10 such as ZSM-5 or ZSM-10 zeolites and also activated carbon. Preferred support materials are aluminum oxides, titanium dioxides, zirconium dioxide and activated carbon.

15 Examples of possible heterogeneous catalysts are the following: platinum dioxide, palladium on aluminum oxide, palladium on silicon dioxide, palladium on barium sulfate, rhodium on activated carbon, rhodium on aluminum oxide, ruthenium on silicon dioxide or activated carbon, nickel on silicon dioxide, nickel on 20 aluminum oxide, nickel on zirconium dioxide, cobalt on silicon dioxide, cobalt on aluminum oxide, cobalt/molybdenum on aluminum oxide, carbonyl iron powder, rhenium black, Raney rhenium, rhenium on activated carbon, rhenium-palladium on activated carbon, rhenium-platinum on activated carbon, copper on silicon 25 dioxide, copper on aluminum oxide, copper on activated carbon, copper on kieselguhr, copper on silica gel, copper on titanium dioxide, copper on zirconium dioxide, copper on magnesium silicate, copper on aluminum silicate, copper on montmorillonite, copper on zeolite, copper/zinc on aluminum oxide, Raney copper, platinum oxide/rhodium oxide mixtures, platinum-palladium on 30 activated carbon, copper chromite, barium chromite, nickel-chromium oxide on aluminum oxide, Raney nickel, cobalt sulfide, nickel sulfide, molybdenum (VI) sulfide, copper-molybdenum(VI)oxide/silicon dioxide/aluminum oxide catalysts, palladium on activated carbon catalysts partially 35 poisoned with selenium or lead and also the catalysts described in DE-A 39 32 332, US-A 3 449 445, EP-A 44 444, EP-A 147 219, DE-A 39 04 083, DE-A 23 21 101, EP-A 415 202, DE-A 23 66 264 and EP-A 100 406.

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Hydrogenation catalysts containing Brönsted and/or Lewis acid centers or basic centers can also be advantageously used in the process of the present invention. When using such catalysts, the further addition of a Brönsted or Lewis acid or bases to the 45 reaction mixture is generally not necessary.

The catalytically active metals themselves, for example, can act as Brönsted or Lewis acid centers if they are not completely reduced to the respective metals in the activation of the catalyst with hydrogen or hydrogen-containing gases. This
5 applies, for example, to the rhenium- and chromite-containing catalysts such as supported rhenium catalysts and copper chromite. In the supported rhenium catalysts, the rhenium is present as a mixture of rhenium metal with rhenium compounds in higher oxidation states, with the latter being able to act as
10 Lewis or Brönsted acids. Furthermore, such Lewis or Brönsted acid centers or basic centers can be introduced into the catalyst via the support material used. Examples of support material containing Lewis or Brönsted acid centers are aluminum oxides, titanium dioxides, zirconium dioxide, silicon dioxide, silicates,
15 clays, zeolites and activated carbon.

For this reason, hydrogenation catalysts used in the process of the present invention are preferably supported catalysts comprising elements of transition groups I, VI, VII and/or VIII
20 of the Periodic Table of the Elements, in particular elements of transition groups I, VII and VIII of the Periodic Table of the Elements, deposited on a support material acting as Brönsted or Lewis acid. Particularly advantageous catalysts are, for example, copper on activated carbon, copper on silicon dioxide, copper on
25 kieselguhr, copper on silica gel, copper on titanium dioxide, copper on zirconium dioxide, copper on magnesium silicate, copper on aluminum silicate, copper on bleaching earth, copper on zeolite, ruthenium on activated carbon, ruthenium on aluminum oxide, ruthenium on silicon dioxide, ruthenium on magnesium
30 oxide, ruthenium on zirconium dioxide, ruthenium on titanium dioxide, palladium on aluminum oxide, palladium on silicon dioxide, palladium on barium sulfate and palladium on activated carbon catalysts partially poisoned with selenium or lead, platinum on aluminum oxide, platinum on silicon dioxide, nickel
35 on zirconium dioxide, nickel on silicon dioxide, nickel on aluminum oxide, nickel-copper on aluminum oxide, cobalt on silicon dioxide, cobalt on aluminum oxide, cobalt-molybdenum on aluminum oxide.

40 Hydrogenation catalysts which themselves have no such Brönsted or Lewis acid centers can have Lewis or Brönsted acid components such as zeolites, aluminum or silicon oxides, phosphoric acid or sulfuric acid added to them. These are generally added in amounts
45 of from 0.01 to 5 % by weight, preferably from 0.05 to 0.5 % by weight and particularly preferably from 0.1 to 0.4 % by weight, based on the weight of the catalyst used.

Other catalysts suitable for hydrogenating the adduct II to give the n-butyl alkyl ether IV are heterogeneous catalysts which comprise complexes of transition metals from groups VIb, VIIb and VIIIb of the Periodic Table of the Elements which can be used for
5 the homogeneous catalysis of this process stage in heterogenized form, for example those in which the transition metal concerned is fixed to a polymeric matrix.

Such polymeric matrices can be resins such as
10 styrene-divinylbenzene resins or phenol-formaldehyde resins to which the relevant ligands serving to complex the transition metal are preferably covalently bound and in turn form complexes with the transition metals concerned and effectively immobilize the latter in this way.

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With the aid of the heterogeneous catalyst mentioned, the hydrogenation of the adduct II to give the n-butyl alkyl ether IV can be carried out either continuously or batchwise.

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If this reaction is carried out in the liquid phase, the heterogeneous catalyst can be either suspended in the liquid reaction medium or preferably arranged in a fixed bed or a plurality of fixed beds. When using a heterogeneous catalyst
25 suspended in the liquid reaction medium, the process can be carried out, for example, in stirred reactors or loop reactors. When a heterogeneous catalyst arranged in a fixed bed is employed, the reaction mixture is generally passed over the fixed catalyst bed in the upflow or downflow mode.

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The hydrogenation can be carried out in adiabatically or isothermally operated reactors. In general, the liquid reaction mixture is here passed over the catalyst at a space velocity of from 0.01 to 10, preferably from 0.05 to 6 and particularly
35 preferably from 0.08 to 3, kg of reaction mixture/l of catalyst·h. When using the heterogeneous catalysts, the reaction can be carried out in the presence or absence of a solvent. Solvents which can be employed are the same solvents which can also be used when the process is carried out with homogeneous
40 catalysis.

In the case of heterogeneous catalysis, the hydrogen is generally added in a molar ratio to the adduct II fed to the reactor of from 1 to 100, preferably from 1.5 to 80, in particular from 2 to
45 40. The hydrogenation of the adduct II to give the n-butyl alkyl ether IV over the heterogeneous catalyst in the liquid phase is generally carried out at from 20 to 400°C, preferably from 30 to

350°C and particularly preferably from 80 to 250°C, and at a pressure of generally from 1 to 300 bar, preferably from 5 to 250 bar, in particular from 20 to 200 bar.

- 5 The liquid reaction product from stage (d) is generally worked up by distillation, as has already been described for the homogeneous catalysts.
- 10 The hydrogenation can also be carried out in the gas phase. For this purpose, it is possible to use reactors customary per se for gas-phase reactions, for example those in which the catalyst is present in a fixed bed or in a fluidized bed. The reactors can be operated adiabatically or isothermally. When using a fixed bed
- 15 arrangement of the catalyst, the catalyst can be arranged in one fixed bed or advantageously, in order to improve the dissipation of the heat of reaction, in a plurality, for example from 2 to 10, preferably from 2 to 5, fixed beds. When using a plurality of fixed catalyst beds or when the reactor is operated
- 20 adiabatically, it can be advantageous, in order to increase the selectivity of the reaction, to lower the temperature of the reaction gas after leaving the preceding fixed bed and before entering the next fixed bed by between-bed cooling of the reaction gas and/or by injection of additional amounts of cool
- 25 reactants such as hydrogen or adduct II between the individual fixed beds. When a plurality of fixed beds is employed, the reaction in the individual fixed beds before the last fixed bed is advantageously carried out only to a partial conversion, for example up to a conversion of from 50 to 98%. If desired, the
- 30 reaction gases can be diluted with a gas which is inert under the reaction conditions, for example nitrogen, saturated hydrocarbons or argon.

In the hydrogenation in the gas phase, the hydrogen is added in a

35 molar ratio to the adduct II fed to the reactor of generally from 1 to 200, preferably from 1.5 to 80 and particularly preferably from 2 to 40. Hydrogen can be fed to the reactor together with the adduct II and/or, divided into a plurality of substreams, at various points on the reactor. In general, the reaction gas

40 consisting essentially of the adduct II, hydrogen and, if desired, an inert gas is passed over the catalyst at a space velocity of from 0.01 to 10, preferably from 0.05 to 5, in particular from 0.07 to 3, kg of reaction gas/l of catalyst·h. The reaction is generally carried out at from 20 to 400°C,

45 preferably from 100 to 350°C and particularly preferably from 150

to 250°C, and at a pressure of generally from 0.5 to 100 bar, preferably from 0.9 to 50 bar, in particular from 1 to 20 bar.

To work up the gaseous reaction product, it can, if desired after
5 depressurization to atmospheric pressure, be introduced directly into a distillation apparatus and there fractionated into its constituents by distillation.

10 For the hydrogenation in the gas phase, it is possible to use essentially the same heterogeneous catalysts which are also employed for the reaction in the liquid phase. Preference is given to using purely inorganic, mineral catalysts in the gas-phase process. Preferred catalysts are, for example,
15 supported catalysts comprising elements of transition groups I, VI, VII and/or VIII, possibly in combination with one or more elements of transition group V, of the Periodic Table of the Elements, in particular elements of transition groups I, VII and VIII of the Periodic Table of the Elements, deposited on a
20 Brönsted or Lewis acid support material or basic support material. Advantageous catalysts are, for example, copper on activated carbon, copper on silicon dioxide, copper on kieselguhr, copper on silica gel, copper on titanium dioxide, copper on zirconium dioxide, copper on magnesium silicate, copper on aluminum silicate, copper on bleaching earth, copper on
25 zeolite, ruthenium on activated carbon, ruthenium on aluminum oxide, ruthenium on silicon dioxide, ruthenium on magnesium oxide, ruthenium on zirconium dioxide, ruthenium on titanium dioxide, palladium on aluminum oxide, palladium on silicon dioxide, palladium on barium sulfate and palladium on activated
30 carbon catalysts partially poisoned with selenium or lead, platinum on aluminum oxide, platinum on silicon dioxide, nickel on zirconium dioxide, nickel on silicon dioxide, nickel on aluminum oxide, nickel-copper on aluminum oxide, cobalt on silicon dioxide, cobalt on aluminum oxide, cobalt-molybdenum on
35 aluminum oxide.

The process of the present invention is explained in more detail with the aid of the flow diagram in the figure which
40 schematically shows an advantageous embodiment.

Via the feedline 1, a mixture of 1,3-butadiene or a butadiene-containing hydrocarbon mixture (3) and an alcohol ROH 1 (4), preferably n-butanol, is introduced into the reactor 2. In
45 the reactor 2, the alcohol ROH 1 is catalytically added on to 1,3-butadiene, with a mixture of the adduct II and III being formed. The reaction product from the reactor 2, which consists

essentially the adducts II and III, high-boiling butadiene derivatives and unreacted 1,3-butadiene and alcohol ROH I, is fed via line 5 to the gas/liquid separator 6 in which gaseous 1,3-butadiene is separated from the liquid constituents of the reaction product and is either returned via lines 7, 8 to the reactor 2 or is conveyed by line 9 to the flare. The liquid mixture obtained in the separator 6 is conveyed via line 10 to the distillation column 11 in which the more volatile adduct III is separated by distillation from the less volatile adduct II and also from any alcohol ROH I still present and high-boiling butadiene derivatives. The adduct III, unreacted alcohol ROH I and any unreacted 1,3-butadiene still present are subsequently returned via line 12 to the reactor 2 where the adduct III is isomerized in the presence of freshly introduced 1,3-butadiene and alcohol ROH I to form the adduct II. As an alternative however, the unreacted alcohol may also be fed together with the adduct II via line 13 to the reactor 14. The low boilers, eg. vinylcyclohexene fed together with the output from reactor 2 to the column 11 are, if desired together with the residual butadiene separated off in the column 11, conveyed via outlet 26 to the flare. In place of a single distillation column 11, it is also possible for a plurality of distillation columns to be connected in series. This enables higher-boiling reaction products eg. alkoxyoctadienes or alkoxydodecatrienes, present in the output from reactor 2 to be separated from the adduct II and removed from the process. Since these compounds do not interfere in the hydrogenation [d], a separation can also be omitted and the alkoxyoctadienes or alkoxydodecatrienes can be fed together with the adduct II via line 13 to the hydrogenation reactor 14.

The liquid output from column 11, which has been freed of the more volatile adduct III and of low-boiling and possibly higher-boiling by-products, is, possibly together with unreacted alcohol ROH I, fed via line 13 to the hydrogenation reactor 14 where the adduct II is hydrogenated in the presence of a homogeneous or heterogeneous transition metal catalyst to give the n-butyl alkyl ether IV. The hydrogen required is fed in via line 15 or 16.

The reaction product from reactor 14, which consists essentially of n-butyl alkyl ether, high-boiling butadiene derivatives, for example octyl alkyl ether or dodecyl alkyl ether plus, if a homogeneous catalyst has been used in the reactor 14, catalyst solution, is fed via line 17 to the distillation column 18.

Unreacted hydrogen is mostly taken off via line 19 and either returned via lines 15 or 16 to the reaction or is conveyed to the flare. If desired, the hydrogen can also be separated off by

means of a gas/liquid separator installed between the reactor 14 and the distillation column 18 and, as indicated above, be reused.

- 5 In the distillation column 18, the hydrogenation product from reactor 14 is separated into its constituents by distillation. Low-boiling by-products are taken off at the top via line 20 and are further purified in an additional distillation stage which is not shown here. The n-butyl alkyl ethers are discharged from the
10 column via line 21, higher-boiling products, for example, octyl alkyl ethers and dodecyl alkyl ethers, are taken off via a plurality of outlets (22) in the lower part of the column 18. If a homogeneous catalyst has been used in the reactor 14, the catalyst solution is taken from the bottom of the column 18 via
15 line 23 and, if desired after bleeding off a substream of used catalyst via line 24 and making up with fresh catalyst solution via line 25, is returned to the reactor 14.

- Although it is already known from US 2 922 822 (Example 1) and
20 from WO 95/19334 that an isomerization can be carried out by separation of the adducts of alcohols with butadiene and recirculation in order to produce only one of the two isomers, neither document states or suggests that alkyl butyl ethers can be successfully prepared in a novel and industrially very
25 advantageous manner by a combination of addition reaction, separation, isomerization and hydrogenation.

Examples

- 30 Example 1 (addition of alcohol onto butadiene and isomerization)
(Subreaction a)

- The preparation of a butyl butenyl ether mixture
35 (3-butoxybut-1-ene and 1-butoxybut-2-ene) was carried out as described in Examples 1 to 4 and 8 to 11 of WO 95/19334.

- The isomerization of adduct III to adduct II in a separate isomerization stage or by returning the adduct of the formula III
40 to stage (a) was carried out as described in Example 5 of WO 95/19334.

Example 2 (Hydrogenation of the adduct II by means of homogeneous catalysis)

- 5 a) An autoclave was charge with 0.25 g of the catalyst
HRuCl(CO)(PPh₃)₃ and 26.95 g (210 mmol) of 1-butoxybut-2-ene
and the mixture was stirred at 150°C for 6 hours under 18 bar
of hydrogen. The reaction mixture was subsequently analyzed
by means of calibrated gas chromatography. At a conversion of
10 92 %, di-n-butyl ether was obtained with a selectivity of
90 %, 1-butoxybut-1-ene with a selectivity of 3 % and
1,1-dibutoxybutane with a selectivity of 4 %.
- 15 b) An autoclave was charged with 0.24 g of the catalyst
HRh(CO)(PPh₃)₃ and 26.95 g (210 mmol) of 1-butoxybut-2-ene and
the mixture was stirred at 150°C for 6 hours under 18 bar of
hydrogen. The reaction mixture was subsequently analyzed by
means of calibrated gas chromatography. At a conversion of
20 82 %, di-n-butyl ether was obtained with a selectivity of
76 %, 1-butoxybut-1-ene with a selectivity of 13 % and
1,1-dibutoxybutane with a selectivity of 8 %.

Example 3 (Hydrogenation of the adduct II by means of heterogenous catalysis in the liquid phase)

- 25 A glass autoclave was charged with 0.1 g of the catalyst
palladium on activated carbon (10%) and 7.0 g (54 mmol) of
1-butoxybut-2-ene. After a reaction time of 3 hours at 100°C under
12 bar of hydrogen, the reaction mixture was analyzed by means of
30 calibrated gas chromatography. At a conversion of 99 %, di-n-butyl ether was obtained with a selectivity of 82 %.

Example 4 (Hydrogenation of the adduct II by means of heterogeneous catalysis in the gas phase)

- 35 A reactor was charged with 100 ml of a nickel/copper/aluminum
oxide catalyst having a nickel content, calculated as NiO, of
50 % by weight and a copper content, calculated as CuO, of 17 %
by weight. The temperature of the catalyst bed was increased to
40 200°C over a period of 2 hours in the presence of activating gas
(2 % hydrogen) at atmospheric pressure. The hydrogen content was
subsequently increased to 25 %, 50 % and 100 % at intervals of 2
hours.
- 45 The reactor was then cooled to 170°C and 24 g/h of
1-butoxybut-2-ene was passed through the reactor at atmospheric
pressure. At the same time, a hydrogen stream of 9.5 l/h was fed

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to the reactor. After cooling, the single-phase, liquid output from the reactor was analyzed by means of calibrated gas chromatography. At a conversion of 99 %, di-n-butyl ether was formed with a selectivity of 99 %.

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We claim:

1. A process for preparing n-butyl alkyl ethers which comprises

a) reacting 1,3-butadiene or a butadiene-containing hydrocarbon mixture with an alcohol of the formula I

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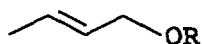
ROH

I,

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where the radical R is a C₂-C₂₀-alkyl, alkenyl, cycloalkyl or cycloalkenyl group, each of which may be unsubstituted or substituted by 1 or 2 C₁-C₁₀-alkoxy or hydroxy groups, a C₆-C₁₀-aryl group or a C₇-C₁₁-aralkyl group or the methyl group, at elevated temperature and elevated pressure in the presence of a Brönsted acid or in the presence of a complex of an element from group Ib, VIIb or VIIIb of the Periodic Table of the Elements with phosphorus- or nitrogen-containing ligands to give a mixture of adducts of the formulae II

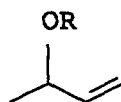
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II

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and III



III ,

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where R is as defined above,

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b) separating the adducts of the formula II and III,

c) isomerizing the adduct III in the presence of a catalyst as indicated for (a) to give the adduct II and

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d) hydrogenating the adduct II in the liquid phase in the presence of a homogeneous or heterogeneous transition metal catalyst or in the gas phase in the presence of a heterogeneous transition metal-containing catalyst to give an n-butyl alkyl ether of the formula IV

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IV.

2. A process as claimed in claim 1, wherein the reaction of
5 1,3-butadiene or a butadiene-containing hydrocarbon mixture
with an alcohol ROH I is carried out in the presence of an
acid ion exchanger.
- 10 3. A process as claimed in claim 1, wherein the reaction of
1,3-butadiene or a butadiene-containing hydrocarbon mixture
with an alcohol ROH I is carried out in the presence of a
catalyst comprising an alkylphosphine, arylphosphine or
15 arylalkylphosphine complex of a transition metal from group
VIIb or VIIIb of the Periodic Table of the Elements.
4. A process as claimed in claim 1, wherein the reaction of
1,3-butadiene or a butadiene-containing hydrocarbon mixture
20 with an alcohol ROH I is carried out in the presence of a
catalyst comprising an alkylphosphine, arylphosphine or
arylalkylphosphine complex of palladium.
5. A process as claimed in claim 1, wherein the isomerization of
25 the adduct III to give the adduct II is carried out in the
presence of a catalyst as is used for catalyzing the addition
of the alcohol ROH I according to the subreaction (a), or the
adduct III is returned directly to the subreaction (a) and is
isomerized there to give the adduct II.
- 30 6. A process as claimed in claim 1, wherein the hydrogenation
(d) is carried out in the liquid phase or the gas phase over
a heterogeneous hydrogenation catalyst.
- 35 7. A process as claimed in claim 1, wherein the hydrogenation
(d) is carried out in the gas phase in the presence of at
least one heterogeneous catalyst comprising one or more
elements from the groups Ib, VIb, VIIb and/or VIIIb of the
Periodic Table of the Elements.
- 40 8. A process as claimed in claim 1, wherein the hydrogenation
(d) is carried out in the presence of at least one
heterogeneous catalyst comprising palladium, nickel or copper
or a mixture of these elements on a support material.

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9. A process as claimed in claim 1, wherein the alcohol ROH I used is n-butanol and is used in stage (a) in an at least one molar excess.

⁵ 10. A process as claimed in claim 1, wherein the reaction, at least in stages (a) to (c), is carried out in the presence of up to 20 % by weight of water, based on the reaction mixture.

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