

Preparation of alkoxybutenes

5 The present invention relates to an improved process for preparing alkoxybutenes by addition of alcohols onto butadiene in the presence of water.

10 1-Alkoxybut-2-enes are sought-after intermediates, eg. for the preparation of n-butyraldehyde and n-butanol according to the process described in WO 95-19 334.

It is known from US 2 922 822 and DE-A 25 50 902 that alcohols react in the liquid phase with 1,3-butadiene in the presence of
15 acid ion exchangers to give the corresponding unsaturated ethers. In US 2 922 822, this reaction is carried out in the presence of a large excess of methanol which leads to increased formation of the undesired dimethyl ether. According to the process of DE-A 25 50 902, vinylcyclohexene is formed as main product in
20 this reaction. According to EP-A 25 240, the addition of alcohols onto 1,3-butadiene is advantageously carried out in the presence of a polar, aprotic solvent which then has to be distilled off again. According to GB-A 943 160, the addition of alcohols is carried out using Brönsted acids in the presence of copper salts.
25 Especially in WO 95-19 334, the addition of alcohols onto butadiene or butadiene-containing mixtures in good yields is described in detail. (That reference also describes how the 1-alkoxybut-2-enes alone can be prepared by isomerization of 3-alkoxybut-1-enes.)

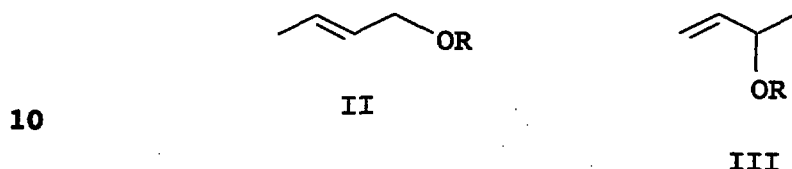
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Nevertheless, these processes always form a large number of dimers or oligomeric derivatives of butadiene or dialkyl ether for which there is virtually no use or which can be employed only in such small amounts that the major part of these by-products
35 which are unavoidably formed in an industrial process would have to be disposed of.

It is an object of the present invention to find a further
40 improvement in the process for preparing alkoxybutenes by addition of alcohols onto butadiene which makes it possible to prepare these products with increased selectivity and yield.

We have found that this object is achieved by a process for
45 preparing alkoxybutenes in which 1,3-butadiene or a butadiene-containing hydrocarbon mixture is reacted with an alcohol of the formula ROH I at elevated temperature and elevated

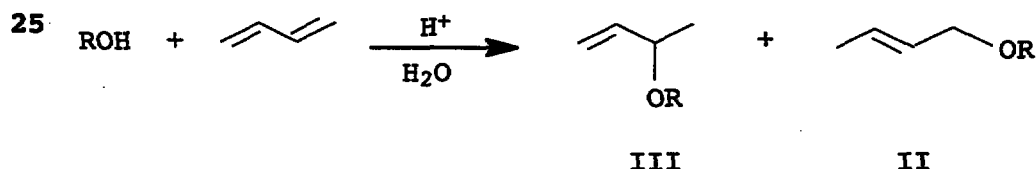
pressure in the presence of a Brönsted acid to give a mixture of the adducts of the formulae II and III, where the radical R is a C₂-C₂₀-alkyl, alkenyl, cycloalkyl or cycloalkenyl group, each of which may be unsubstituted or substituted by 1 or 2 C₁-C₁₀-alkoxy 5 or hydroxy groups, a C₆-C₁₀-aryl group or a C₇-C₁₁-aralkyl group or the methyl group,



wherein the improvement comprises carrying out the reaction in the presence of water, eg. up to 20 % by weight of water, based 15 on the liquid reaction mixture.

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

20 In the reaction, 1,3-butadiene or a butadiene-containing hydrocarbon mixture is reacted in the presence of water and a Brönsted acid with the alcohol ROH I according to the equation



30 to give the 1,4-adduct of the formula II and the 1,2-adduct of the formula III. The double bond in the resulting 1,4-adduct II can be in either the cis or trans configuration. The adducts II and III are generally formed, depending on the reaction 35 conditions and the catalyst used, in a molar ratio of from 1:1 to 1:3.

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 40 secondary alcohols, but preference is given to using primary alcohols. Either aliphatic, cycloaliphatic, aromatic or araliphatic alcohols can be employed, but preference is given to using aliphatic or araliphatic alcohols. In general, the alcohols ROH I used in the process of the present invention are ones in 45 which the radical R is a C₁-C₂₀-alkyl group, C₂-C₁₀-alkenyl group, eg. the but-2-enyl group, preferably a C₁-C₄-alkyl group, in particular the n-butyl group, a C₁-C₂₀-cycloalkyl group or

cycloalkenyl 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 substituents such as C₁-C₁₀-alkoxy and/or hydroxyl groups. The alcohols ROH I
5 used can thus also be diols or triols or alkoxy alcohols. Since these substituents generally have no critical influence on the reaction, preference is given to using alcohols ROH I having unsubstituted radicals R. Of course, it is also possible to use alcohols having a higher number of carbon atoms. Since such
10 higher alcohols are generally more expensive than lower alcohols, mostly lower alkanols and in particular butanol are preferably used for economic reasons.

Brönsted acids used for the addition of alcohols ROH I onto
15 1,3-butadiene or butadiene-containing hydrocarbon mixtures are, for example, conventional, nonoxidizing Brönsted acids such as hydrohalic acids, eg. hydrochloric acid, sulfuric acid, phosphoric acid, perchloric acid, hydrofluoric acid, tetrafluoroboric acid, methanesulfonic acid or toluenesulfonic
20 acid, but preference is given to using solid Brönsted acids, in particular organic cation exchangers.

For the purposes of the present invention, organic cation
25 exchangers are pulverulent, gel-like or macroporous, polymeric polyelectrolytes bearing Brönsted acid functional groups such as sulfonic acid, phosphonic acid or carboxyl groups on a polymeric matrix, for example sulfonated phenol-formaldehyde resins, sulfonated styrene-divinylbenzene copolymers, sulfonated
30 polystyrene, poly(perfluoroalkylene)sulfonic acids or sulfonated coals. These cation exchangers can be used in the form of commercial products as are commercially available under the trade names Amberlite®, Dowex®, Amberlyst®, Lewatit®, Wofatit®, Permutit®, Purolite® and Nafion®. The cation exchangers are
35 advantageously employed in their protonated form, referred to as the H⁺ form. Examples of suitable organic cation exchangers are the commercial products Amberlite® 200, Amberlite® IR 120, Amberlite® IR 132 E, Lewatit® SC 102, Lewatit® SC 104, Lewatit® SC 108, Lewatit® SPC 108, Lewatit® SPC 112, Lewatit® SPC 118, Purolite® CT 175, Purolite® CT 171, Amberlyst® CSP 2 and
40 Amberlyst® 15.

These are preferably arranged in a fixed bed and the liquid reaction mixture flows through them in the upflow or downflow
45 mode. The fixed catalyst bed can be installed, for example, in tube reactors or preferably in reactor cascades. It is also possible to pass the reactants in gaseous form through the

catalyst bed, but preference is given to working in the liquid phase. It is self-evident that the addition of the alcohol ROH onto 1,3-butadiene or butadiene-containing hydrocarbon mixtures can be carried out either continuously or batchwise.

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The molar ratio of alcohol/1,3-butadiene can be selected from within a wide range. The molar ratio of alcohol ROH/1,3-butadiene generally employed is from 0.5:1 to 5:1, preferably from 1:1 to 2.5:1 and particularly preferably from 1.5:1 to 2.5:1. The
10 reaction of the alcohol ROH I with 1,3-butadiene or butadiene-containing hydrocarbon mixtures is generally carried out at from 20 to 150°C, preferably from 50 to 120°C, in particular from 70 to 110°C, and at a pressure of generally from 1 to 100 bar, preferably from 3 to 50 bar, in particular from 5 to
15 20 bar. The use of a higher pressure is possible. The reaction temperature employed is advantageously optimized in a preliminary experiment for the Brönsted acid catalyst used in each case.

20 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 0.02 to 0.4 g/cm³·h and particularly preferably from 0.02 to 0.05 g/cm³·h. The addition of a solvent to the reaction mixture is possible but generally not
25 necessary since the alcohol used as well as the adducts II and 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 is, as a rule, dependent on the reaction temperature employed.

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In place of pure 1,3-butadiene, it is also possible to use 1,3-butadiene-containing hydrocarbon mixtures as raw material. Such hydrocarbon streams are obtained, for example, as C₄ fraction in steam crackers. Before use, these hydrocarbon streams are
35 advantageously freed of any acetylenic or allenic hydrocarbons present therein by partial hydrogenation (Weissermel, Arpe: Industrielle Organische Chemie; 3rd Edition, VCH Verlagsgesellschaft, Weinheim 1988). The 1,3-butadiene-containing hydrocarbon streams can then be introduced in a similar manner to
40 pure 1,3-butadiene. Advantageously, the saturated or monoolefinic hydrocarbons which are present in these hydrocarbon streams and have not reacted in the reaction are removed from the reaction product, for example by means of a gas/liquid separator.

45 It has now been surprisingly found that addition of water gives an increase in selectivity and thus also an increase in yield.

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To prepare the alkoxybutenes, water is added to the reaction mixture in a proportion by weight of generally from 20 % by weight to 0.0001 % by weight, preferably from 10 to 0.001 % by weight and particularly preferably from 5 to 0.01 % by weight, based on the liquid reaction mixture. When the process is carried out batchwise, the reactor can be initially charged with the water together with the other reactants, but it can also be advantageous to meter the water into the reactor only after the reaction has commenced. Which of these procedures is selected in the end depends on the catalyst used in the particular case and the pressure and temperature conditions employed. The optimum procedure is advantageously determined in a preliminary experiment for the catalyst used in the particular case. In a similar way, when the process is carried out continuously, eg. in a tube or cascade reactor, the water can be introduced into the reactor together with the other reactants or else metered into the reactor via a separate inlet only after a certain residence time of the reactants in the reactor. In a further embodiment of the process of the invention, the water can, instead of being metered into the reaction mixture, also be introduced into the reaction mixture by use of water-moist ion exchangers and the proportion of water can be increased or lowered if necessary by metered addition of fresh water or removal of a certain amount of water.

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Examples

Example 1 (Reaction without water)

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A 0.3 l stirring autoclave was charged with 65.7 g (0.89 mol) of n-butanol and 15.0 g of Purolite[CT 175 in the H^+ form which had previously been washed with water and acetone and dried in a stream of nitrogen. Subsequently, 33.2 g (0.61 mol) of 1,3-butadiene were injected into the reactor. After a reaction time of 10 hours at 90°C and a pressure of 9 bar, a selectivity of 40.8 % of 3-butoxybut-1-ene, 40.9 % of 1-butoxybut-2-ene, 11.7 % of butoxyoctadienes and 3.4 % of dibutyl ether was obtained at a conversion of 73 %, ie. a total yield of alkoxybutenes of 59.6 %.

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Example 2 (Reaction in the presence of water)

A 0.3 l stirring autoclave was charged with 65.7 g (0.89 mol) of n-butanol, 1.2 g of water and 15.0 g of Purolite[CT 175 in the H^+ form which had previously been washed with water and acetone and dried in a stream of nitrogen. Subsequently, 38.0 g (0.70 mol) of 1,3-butadiene were injected into the reactor. (The fact that the

amount of butadiene is different from Example 1 is a coincidence, since exact metering is not possible during injection. The slightly different amount does not influence the yield.) After a reaction time of 10 hours at 90°C and a pressure of 9 bar, a selectivity of 45.2 % of 3-butoxybut-1-ene, 42.5 % of 1-butoxybut-2-ene, 5.9% of butoxyoctadienes and 1.1 % of dibutyl ether was obtained at a conversion of 71 %, ie. a total yield of dialkoxybutenes of 62.3 %.

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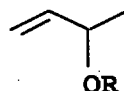
We claim:

1. A process for preparing alkoxybutenes by reacting 1,3-butadiene or a butadiene-containing hydrocarbon mixture with an alcohol of the formula ROH I at elevated temperature and at elevated pressure in the presence of a Brönsted acid to give a mixture of the adducts of the formulae II and III

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II



III

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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, or a C₂-C₁₀-aryl group or a C₇-C₁₁-aralkyl group or the methyl group, wherein the reaction is carried out in the presence of water.

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2. A process as claimed in claim 1, wherein the reaction is carried out in the presence of up to 20 % by weight of water, based on the liquid reaction mixture.

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3. A process as claimed in claim 1, wherein the reaction is carried out in the presence of from 0.001 to 10 % by weight of water, based on the liquid reaction mixture.

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4. A process as claimed in claim 1, wherein the reaction is carried out in the presence of from 0.01 to 5 % by weight of water, based on the liquid reaction mixture.

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5. A process as claimed in claim 1, wherein the alcohol ROH I used is n-butanol.

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