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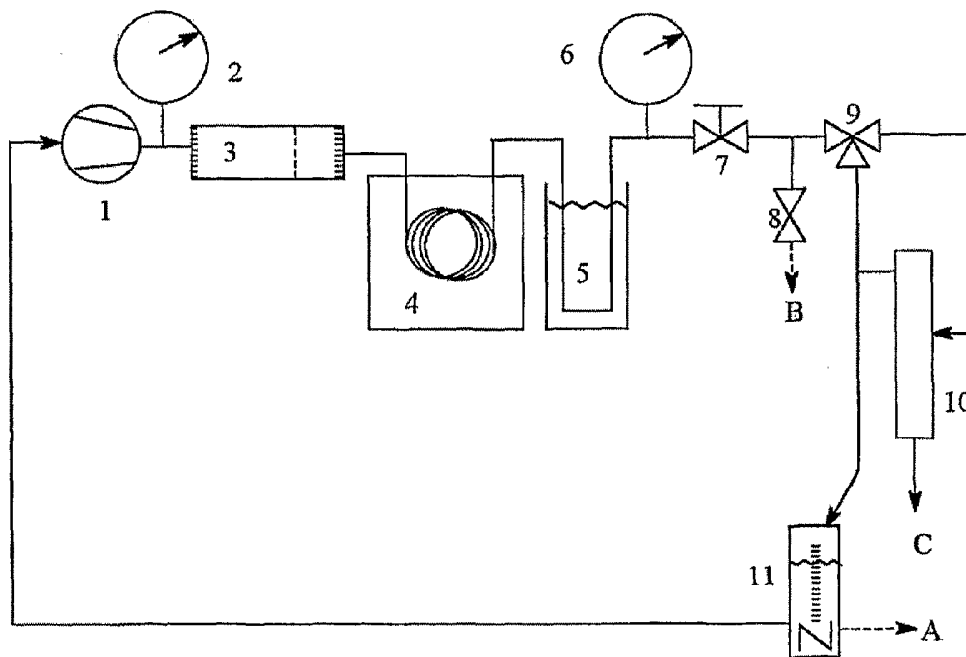
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(54) Title: METHOD FOR THE ADDITION OF FORMALDEHYDE TO OLEFINS



(57) Abstract: The invention relates to a method for the manufacture of non-saturated homoallyl alcohols and their formiates by the conversion of formaldehyde with an olefin or an olefin mixture.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD FOR THE ADDITION OF FORMALDEHYDE TO OLEFINS

Object of the invention is a method for the manufacture of non-saturated homoallyl alcohols and their formiates by the conversion of formaldehyde with an olefin or an olefin mixture.

Fatty alcohols are used for the manufacture or use in a large number of products, such as, for example, wash-active substances, emulsifiers, rolling oils and cosmetic raw materials. In this situation, the fatty alcohols are used as such, or in the form of their derivatives, e.g. in the form of their esters and ethers. Fatty alcohols are an important chemical intermediate product for the manufacture of carboxylic acids, guerbet alcohols, amines, acetals, ethoxylates, and ether sulphates.

The chemical-physical properties and their biodegradability, or the biodegradability of the subsequent products of the fatty alcohols are determined quite substantially by the length of the chain. The oxidation of the corresponding aldehydes plays a part in particular with chain lengths of C_6 to C_{10} , since these aldehydes can be used as scent and taste substances. The provision of smell and taste changes with the chain length, with the result that a specific pure representation of the aldehydes is also of economic significance.

A series of methods are already known from practice which lead to saturated or non-saturated fatty alcohols. Fatty alcohols can be obtained from native sources in the form of fats and oils by saponification and reduction. The natural sources of raw materials quite predominantly exhibit chain length compositions from C_{12} to C_{22} , as a result of which their range of application is limited. In the tenside sector in particular, due to their cold washing properties, for example, chain lengths from C_{12} to C_{14} are required, for which predominantly coconut oil and palm oil of natural origin come into consideration. The fatty alcohols derived from natural sources or their derivatives additionally exhibit a chain length distribution.

The manufacture of alcohols by the addition of formaldehyde with double bonds has long been known. According to the Prins reaction, aldehydes are condensed to olefins in the presence of strong mineral acids or organic acids as the catalyst. A disadvantage of the reaction is that, under the reaction conditions, the olefins used isomerise and predominantly form 1,3 diols and dioxanes.

The poor yields and selectivities can be improved by the choice of suitable solvent media.

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In addition, Lewis acids have been proposed as catalysts for the addition of formaldehyde and metal salts, metal carbonyls, and fluorinated aluminium compounds (US 4,039,594) and bases (US 3,574,773) as additional catalysts.

5 In addition to this, the thermal conversion of olefins with formaldehyde is known (US 2,335,027). Without further measures, however, it is only possible for reactive terminal stage 1,1-disubstituted olefins and middle-stage 1,2-disubstituted olefins with low yields to be converted, since otherwise defined solvents, organic acids, or other promoters must be added in order to achieve acceptable yields and selectivities.

10 The methods cited above are described, for example, in B.B. Snider, Comprehensive Organic Synthesis; Editor B.M. Trost and I. Fleming, Pergamon Press 1991, Vol. 2; pp. 527-561. Common to all the methods is a high loss of formaldehyde, the formation of methanol, and free formic acid, which are formed by disproportioning from formaldehyde.

15 The presence of formic acid leads in addition to the isomerisation of the olefins and, if applicable, to the formation of formic acid methyl ester and the formic acid esters of the homoallyl alcohols. In addition to this, by-products are incurred by the second addition of formaldehyde. In all the methods which use catalysts such as Lewis acids, the catalysts must be separated in additional process stages from the reaction mixtures and, if
20 appropriate, regenerated.

Only oxosynthesis under the use of metal organic cobalt, rhodium, and ruthenium catalysts has found an industrial application. Known disadvantages of these are the high price of the catalysts and the difficult purification of the product mixture of 2-alkyl-
25 branched and linear aldehydes.

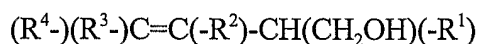
There is accordingly a need for a direct addition method for adding formaldehyde to olefins, in which the elaborate separation and regeneration of catalysts can be done away with, and primary alcohols can be obtained, and which can be converted simply and
30 specifically to saturated alcohols, such as fatty alcohols, with defined chain lengths and/or branching, or the derivatives of these.

The known technical methods for the manufacture of fatty alcohols, with the use of formaldehydes and non-saturated compounds, exhibit disadvantages which are based on
35 the elaborate process performance, and/or lead to product mixtures which do not allow for a specific manufacture of defined chain lengths. Other known methods use catalysts and reagents which make the methods uneconomical, or lose a large part of the formaldehyde

used due to disproportionising, which then means that this is lost for the addition reaction. In addition to this, many of the known manufacturing methods exhibit poor yields and selectivities.

5 The problem of the invention is to provide a method which overcomes the disadvantages of the prior art outlined above, and which adds only one formaldehyde unit selectively to the double bond of a non-saturated compound.

10 The problem is solved according to the invention by a method for the manufacture of non-saturated homoallyl alcohols, in particular non-saturated homoallyl alcohols of the formula



and the formiates thereof, by conversion of formaldehyde with an olefin of the formula



or a mixture thereof,

whereby R^1 , R^2 , R^3 and R^4 independently of one another are hydrogen or a hydrocarbon residue with 1 to 26 carbon atoms, which optionally can be functionalised and/or two or more can be part of one or more cyclic rings,

20 essentially in the absence of water, whereby the method comprises the steps:

(A) preparing of monomeric formaldehyde containing a water content of less than 1.5 % by weight, preferably less than 1 % by weight, preferably outside the reactor, into which the formaldehyde with the olefin is added, obtainable by the drying the formaldehyde and/or the formaldehyde-precursor compound if the limiting value of 1.5 % by weight, respectively

25 1 % by weight, of water in the formaldehyde is exceeded,

(B) contacting the monomeric formaldehyde with the olefin or olefin mixture, preferably before introduction into the reactor, whereby the olefin is present preferably in fluid form, and/or independently preferred, formaldehyde and olefin are of the same phase,

30 (C) reacting the formaldehyde with the olefin at temperatures of from 200 to 300 °C, preferably from 240 to 280 °C, and more preferred from 245 to 265 °C, and pressures of from 5 to 80 bar, preferably from 15 to 35 bar in one or more reactors, and

35 (D) separating the non-converted olefin and feeding the non-converted olefin back into the reactor/reactors.

The conversion takes place essentially in the absence of water, whereby the expression "essentially in the absence of water" in the meaning of the invention signifies that not more than 1.5 % by weight of water is present during the conversion, and for preference not more than 1 % by weight of water.

5

Preferred embodiments of the invention are the object of the sub-claims.

At the addition of formaldehyde to the terminal olefins, according to the method according to the invention, non-saturated linear homoallyl alcohols are obtained, extended by one C1
10 unit, with a terminal hydroxy group ($R^1 = H$, $R^2 = H$, $R^3 = \text{alkyl}$, and $R^4 = H$). The double bond is displaced in the chain by one carbon atom, and an E/Z isomer mixture is obtained.

At the addition of formaldehyde to internal 1,2-disubstituted olefins ($R^1 = \text{alkyl}$, $R^2 = H$,
15 $R^3 = \text{alkyl}$, and $R^4 = H$), non-saturated defined-branched homoallyl alcohols are obtained with hydroxymethyl side chain ($-\text{CH}_2\text{OH}$). The double bond is displaced along the chain by one bond in relation to the branching position (the equivalent of a carbon atom being added to the formaldehyde). Two defined regioisomers are obtained. An E/Z isomer mixture of each regioisomer is obtained.

At the addition of formaldehyde to the terminal 1,1-disubstituted olefins ($R^1 = H$, $R^2 =$
20 alkyl , $R^3 = \text{alkyl}$, and $R^4 = H$), according to the method according to the invention, non-saturated defined-branched homoallyl alcohols are obtained, extended by one hydroxymethylene side chain. The formaldehyde synthon added to the non-substituted carbon atom and the double bond is displaced by one carbon atom away from the addition
25 position, and is located in the branching position. Two regioisomers are obtained. For each regioisomer one E/Z isomer mixture is obtained.

As olefins, according to the invention, Alk-1-ene, 1,1-di-alkyl-substituted and/or 1,2-di-
30 alkyl-substituted or even cyclic olefins can be used, which in the allyl position carry at least one hydrogen atom or mixtures thereof. As compounds, mention may be made of: 1-octene, from the dimerisation of 1-olefins, or the dehydration of olefins containing guerbetal alcohols or non-saturated fatty acid esters, such as oleic acid.

The conversion in the flow tube reactor (flow pipe reactor) is carried out for preference
35 without the addition of solvents, catalysts, bases, buffers, and/or other additional promoters.

Suitable formaldehyde sources which can be used for the preparation of monomer formaldehyde, in accordance with method step (A), as appropriate containing a water content of less than 1.5 % by weight, for preference less than 1 % by weight, are dried paraformaldehyde, trioxane and methanol, for preference paraformaldehyde and methanol, and for particular preference methanol.

Drying is effected for preference by means of chemical or physical drying means, such as calcium chloride and phosphorpentoxide (P_2O_5) or molecular sieves.

It is of particular advantage to operate in one pressure range during the production of the gaseous formaldehyde, which is above the pressure which prevails in the subsequent method steps, in particular if the reaction is carried out in a flow tube as a reactor. In the flow tube, with a defined setting of an overflow valve at the reactor output, the pressure is a function of the flow rate.

The gaseous flow of monomer formaldehyde is released by water. This can be effected by adsorption to suitable inorganic adsorbents, in particular to molecular sieves, or it can be effected by chemical bonding to suitable drying media, which enter into a chemical bond with water. The use of physical drying processes is likewise possible.

In addition to this, aluminium alcoholates, such as methyl aluminium 2,6-diphenyl phenoxides (Yamamoto et al., JACS 1993, 115, 3943-3949; Yamamoto et al., JACS 1990, 112, 7422-7423) can be used for the activation and stabilization of formaldehyde. Activation is effected taking trioxane as a basis, or monomer formaldehyde obtained by the thermal decomposition of paraformaldehyde, as a monomer or unimolecular formaldehyde by means of the proposed aluminium alcoholates.

A number of process methods for the manufacture of monomer formaldehyde are described hereinafter, and reference is made in addition to: "Faith, Keyes & Clark's industrial Chemicals, F.A. Lowenheim, M.K. Moran Ed., Wiley Interscience, New York, 4th Ed. 1975, 422-429.

(A.1) Formaldehyde from paraformaldehyde

Paraformaldehyde can be thermally decomposed, for example, by heating to a temperature of 120 to 270 °C, in particular to a temperature of 160 to 240 °C, to monomer gaseous formaldehyde. The decomposition of paraformaldehyde can be effected at pressures from 0 bar to 150 bar, for preference at pressure ranges between 10 and 70 bar, and in particular

between 30 and 50 bar.

Paraformaldehyde contains up to 5 % by weight of water. The water is removed from the gas flow by the drying process referred to.

5

The manufacture of formaldehyde which is free of water/low in water and in gaseous form can be effected, for example, by the thermal decomposition of low-molecular paraformaldehyde units in the presence of powerful water extraction media, such as P_2O_5 , such as is described, for example, in DE 1 070 611.

10

(A.2) Formaldehyde from trioxane

Trioxane can be broken down in the first method step by heating to a temperature of 200 to 300 °C, and in particular to a temperature from 250 to 280 °C, to monomer gaseous formaldehyde. The decomposition of trioxane can be effected at pressures from 5 to 150 bar. Particularly preferred pressure ranges are between 10 and 80 bar, and in particular between 20 and 70 bar.

15

Technical trioxane frequently contains water, e.g. about 1 % by weight of water. The gaseous flow of monomer formaldehyde, provided that it contains less than 1.5% by weight of water, therefore does not need to be freed of water traces.

20

(A.3) Formaldehyde from methanol

Methanol can be decomposed in the first method step by dehydration or oxy-dehydration, under partial combustion of the methanol used, in accordance with known methods at 600 to 720 °C to monomer gaseous formaldehyde. The gas flow may contain water. The gaseous flow of monomer formaldehyde, inasmuch as it contains water, is freed from the water as described heretofore, and for preference after it has been cooled to less than 170 °C.

25

The formaldehyde is brought in contact with the olefin in method step (B), the olefin being present in essentially fluid form, for example by the formaldehyde being condensed into the fluid olefin mixture. This can be carried out at normal pressure or under-pressure. In a particularly preferred embodiment, the formaldehyde is fed in by means of reactor inlets at several points on the flow tube reactor. Condensing in under pressure and at increased temperature is of particular advantage. The molar ratio of formaldehyde to olefin at the intake of the flow tube reactor is for preference 0.01 : 1 to 0.5 : 1, in particular 0.03 : 1 to 0.3 : 1, and most particularly 0.04 : 1 to 0.25 : 1.

30

35

The term "condensing in" is understood to mean that the formaldehyde in gaseous form is rendered fluid, for example by increasing the pressure, i.e. it is condensed, and the fluid formaldehyde is mixed into the fluid olefin flow and/or dissolves in it. For preference, the formaldehyde gas flow is condensed into the olefin which is to be converted before the educt flow passes into the reactor, which for preference is a flow tube reactor.

In a further embodiment of the method, trioxane at increased temperature, for preference between 10 and 70 °C, in particular between 40 and 65 °C, is dissolved in the olefin before the educts pass into the reactor, which in this embodiment is designed as a flow tube reactor. The dissolving can take place under pressure. This is particularly necessary if the boiling point of the olefin used lies below the temperature which is required for the dissolving of the trioxane. The monomer formaldehyde is in this case first produced in the flow tube.

The monomer gaseous formaldehyde is for preference condensed into the olefin or formed immediately before the reactor intake, or, in the case of a flow tube reactor, in the front area of the reactor. For preference, the condensing of the formaldehyde takes place in the olefin (B) before the reactor intake. The condensation takes place for preference at a pressure from 10 to 250 bar, and in particular from 20 to 80 bar.

Surprisingly, better yields and better selectivity was found with the thermal addition of formaldehyde to olefins, if monomer formaldehyde passes into the flow tube reactor and is brought to reaction. If the preparation of monomer formaldehyde first takes place due to thermal decomposition of formaldehyde sources in the flow tube reactor, much poorer yields and selectivity is obtained.

In the third method step, the formaldehyde is brought to reaction (C) with the olefin or the olefin mixture at temperatures from 200 to 300 °C. It can be seen that, according to the method according to the invention, the thermal addition of formaldehyde to olefins in a continuous flow tube reactor provides better yields and selectivity than if formaldehyde and olefin are brought to reaction in an autoclave.

The preferred reaction temperatures for the formaldehyde addition in the flow tube reactor lie in a range between 200 and 300 °C, in particular in a range between 240 and 290 °C, and most especially to advantage in a range between 250 and 270 °C. For preference, the reactor is operated in a pressure range which is dimensioned such that the reaction mixture

in the flow tube reactor is fluid and/or single-phase. Surprisingly, specifically with the setting of a single-phase fluid phase in the reactor, particular advantages are obtained with regard to the yield and selectivity of the reaction.

5 It may be of advantage for the reaction temperature in the temperature ranges given above to be adjusted (such as may be possible) in such a way that it lies above the critical temperature of the olefins used, so that a uniform over-critical phase pertains in the flow tube reactor.

10 In general, elevated pressures in the flow tube reactor are preferred. It is also possible, however, for operations to be carried out at such low pressures that a uniform gaseous phase pertains in the flow tube reactor.

15 The conversion values of the olefin which are achieved in the flow tube reactor, with conversion in accordance with the method according to the invention, i.e. with the corresponding setting of the reaction parameters, lie for preference between 1 % and 15 %, and in particular 2 to 10 %.

20 It has surprisingly been shown in some cases that, with the increasing conversion of the olefin and with a rising fraction of homoallyl alcohol in the reaction solution, the selectivity of the reaction, related to the converted olefin, runs through a maximum value and then decreases. The selectivity achieved with one single pass in the continuous flow tube reactor at reaction temperatures from 245 to 260 °C and conversion rates of between 3 % and 8 % of the olefin, lay at 95 to 99 % selectivity. The selectivity achieved, related to
25 the conversion of the formaldehyde introduced, lay between 80 and 88 % under these conditions.

It has surprisingly been shown that a continuous infeed of formaldehyde into the flow tube reactor has a positive effect on the selectivity of the reaction, in particular in relation to the
30 converted formaldehyde. For preference, the flow tube reactor can also exhibit more than one infeed point for formaldehyde into the flow tube reactor, for preference in the front area of the flow tube reactor.

35 The flow tube reactor can also be subdivided into individual sections, which in each case exhibit formaldehyde infeed points. For preference, the flow tube reactor is operated isothermically.

In method step (D), the reaction flow, which for preference is relaxed by means of a flow resistance, is subjected to a separation process, which is suitable for separating light volatile components and heavy volatile components from the non-converted olefins. A preferred separation method is distillation. Other methods of separation, such as adsorption, can also be used. Distillation can be carried out in a rectification column, for preference in two rectification columns.

With the use of two rectification columns, the following process sequences are possible.

Variant One: From the head of the first column are drawn the components which have a lower boiling point than the olefin used or the olefin mixture used. From the sump of the column are drawn the non-converted olefin and the reaction products with higher boiling points, which are then conducted to the second reaction column.

From the head of the second column are drawn the non-converted olefins or the non-converted olefin mixture, and from the sump of the second column are drawn the reaction products which contain the main constituents of the homoallyl alcohol formed.

Variant Two: From the head of the first column are drawn the components which have a lower boiling point than the olefin used, and the non-converted olefin is also drawn off. This fraction is transferred to the second column. Drawn from the sump of the second column are the reaction products which contain the homoallyl alcohols formed as the main constituents. Drawn from the head of the second column are the components which have a lower boiling point than the olefin used. From the sump of the column is drawn the non-converted olefin. The non-converted olefins, separated by a suitable separation method, can be conducted back and introduced into the educt flow at the intake of the flow tube reactor.

The homoallyl alcohol manufactured by the method according to the invention is well-suited for being hydrated into saturated fatty alcohol, in whole or in part, in a downstream hydrating process.

It has surprisingly been shown that, by means of the linking and arrangement according to the invention of the process steps and process parameters, on the one hand a flexible use of 1,1-disubstituted olefins and in particular 1-olefins and 1,2-disubstituted olefins is made possible, and, on the other, a high selectivity with good yield is achieved. The method is characterised in that the addition of formaldehyde to the olefins used does not require the

use of a catalyst and/or a solvent, and for preference takes place free of these.

The method is applied for preference in continuous operation. It is also possible for it to be subdivided into method steps, which individually or as a whole can be carried out as discontinuous method steps or processes. With sufficient dimensioning of the individual parts of the system, the proposed method allows for the manufacture of a variable product volume with constant product composition.

The conversions according to Examples 1 to 4 are explained by way of example on the basis of Figure 1. The conversions according to Examples 5 to 8 are carried out in a laboratory apparatus in accordance with Figure 2.

Example 1

Addition of formaldehyde to 1-octene, formaldehyde source paraformaldehyde.

Paraformaldehyde (II) was converted into monomer gaseous formaldehyde (I) at 240 to 280 °C in a heated decomposition apparatus (1). The gas pressure incurred was higher than the intake pressure of the flow tube reactor (4). Paraformaldehyde (II) was introduced continuously into the decomposition apparatus (1). The formaldehyde gas flow (I) was conducted via the dryer (2), which reduced the water content of the gaseous formaldehyde to less than 1.5 %. 1-octene (IV) was delivered via the pump (3) into the heated flow tube reactor (4). The pressure in the flow tube reactor was regulated to 30 bar by means of a regulatable flow resistance in the form of a valve (5) at the outlet of the flow tube reactor, and the temperature of the flow tube reactor brought to 250 °C.

The dried formaldehyde gas flow (III) was introduced at the start of the flow tube reactor in a molar ratio of 0.1 : 1 (formaldehyde : 1-octene). The mean dwell time in the reactor was 30 minutes.

The emergent reaction mixture (V) was relaxed after the valve (5) and cooled in a heat exchanger (6). The cooled reaction mixture (XII) was freed of light boiling constituents such as methanol (VI) and inert gas constituents in a distillation column (7). The heavy boiling constituents, consisting of the non-converted 1-octene and 3-nonen-1-ol and 3-nonen-ol-formiate (VII), passed into the second distillation column (8). From the head of the column was drawn 1-octene(VII), and conveyed back to the intake of the flow tube reactor. From the sump of the columns are drawn 3-nonen-1-ol and 3-nonen-1-ol-formiate (IX). The product flow (IX) is suitable for being converted into fatty alcohols in the

subsequent process steps (9) by saponification and/or catalytic hydration. Further processing into further derivatives can be added.

Example 2

5 Addition of formaldehyde to 1-octene, formaldehyde source trioxane

10 Trioxane (II) was converted into monomer gaseous formaldehyde (1a) at 270 to 300 °C in a heated decomposition device (1). The gas pressure was above the intake pressure of the flow tube reactor. New molten trioxane (II) was introduced continuously into the decomposition device. The formaldehyde gas flow (I-a) was introduced into the flow tube reactor (4), circumventing the dryer.

15 1-octene (IV) was conveyed via the pump (3) into the heated flow tube reactor (4). The pressure in the flow tube reactor was regulated to 30 bar by means of a regulatable flow resistance in the form of a valve (5) at the output of the flow tube reactor. The temperature of the flow tube reactor was set at 250 °C. The further procedure corresponded to Example 1.

Example 3

20 Addition of formaldehyde to 1-octene, formaldehyde source methanol

Methanol was dehydrated at 600 to 720 °C in accordance with existing processes (1) and converted to monomer gaseous formaldehyde (I).

25 A gas pressure was built up which was above the intake pressure of the flow tube reactor. New methanol (II) was introduced continuously into the dehydration apparatus (1). A hydrogen flow (XI) was drawn from the dehydration apparatus. The formaldehyde gas flow was conducted via a dryer (2), which reduced the water content in the gaseous formaldehyde to less than 1.5 %.

30 1-octene (IV) was conveyed via a pump (3) into the heated flow tube reactor (4), and the pressure in the flow tube reactor regulated to 30 bar by means of the regulatable flow resistor in the form of a valve (5) at the outlet of the flow tube reactor. The temperature of the flow tube reactor was set at 250 °C.

35 The dried formaldehyde gas flow (III) was introduced at the start of the flow tube reactor in a molar ratio of 0.1 : 1 (formaldehyde : 1-octene). The mean dwell time in the reactor

was 30 minutes. The further procedure corresponded to Example 1.

Example 4

Addition of formaldehyde to 4-octene, formaldehyde source paraformaldehyde

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Paraformaldehyde was converted into gaseous formaldehyde as in Example 1 and fed into the flow tube reactor. 4-octene (IV) was delivered by means of a pump (3) into the heated flow tube reactor (4), and the pressure in the flow tube reactor regulated to 30 bar by means of a regulatable flow resistance in the form of a valve (5) at the outlet of the flow tube reactor. The temperature of the flow tube reactor was set at 250 °C.

15

The dried formaldehyde gas flow (III) was introduced at the start of the flow tube reactor in a molar ratio of 0.2 : 1 (formaldehyde : 4-octene). The mean dwell time in the reactor was 30 minutes.

20

The emergent reaction mixture (V) was relaxed after the valve (5), cooled in the heat exchanger (6), and freed in the distillation column (7) of light boiling constituents such as methanol (VI) and inert gas constituents in a distillation column (7). The heavy boiling constituents, consisting of the non-converted 4-octene and 5-hydroxymethylene-3-octene and 5-hydroxymethylene-3-octene-formiate (VII), passed into a second distillation column (8).

25

From the head of the column 4-octene (VIII) was drawn, and conveyed back to the intake of the flow tube reactor. From the sumps of the columns were drawn 5-hydroxymethylene 3-octene and 5-hydroxymethylene 3-octene-formiate (IX). The product flow (IX) is suitable for conversion in subsequent process stages (9) into fatty alcohols by saponification and/or catalytic hydration. Further processing into further derivatives can be added.

30

Example 5

Thermal addition of formaldehyde to 1-octene

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1-octene was pumped by a high-pressure pump (1) from a reservoir (11) with gradation through the steel capillaries (4) located in the furnace, and with their temperatures adjusted as a result. By means of the needle valve (7) a pressure of 23 to 35 bar was set at the output of the steel capillaries. The delivery capacity of the pump was 0.2 to 3 ml/min. In the temperature-controlled decomposition apparatus (3), paraformaldehyde dried by P₂O₅

was presented.

The steel capillaries were brought to a temperature of between 245 and 255 °C. Once the temperature had been reached, the decomposition apparatus was continuously heated from 140 to 230 °C. The monomer formaldehyde continuously discharged from the decomposition apparatus was carried by the fluid flow of 1-octene into the steel capillaries. The flow speed was adjusted in accordance with the decomposition temperature in the decomposition apparatus and the reaction temperature in the capillaries, in such a way that no more formaldehyde could be demonstrated at the outlet of the steel capillaries by means of the sampling valve (8). The reaction solution discharged passed, after cooling (5), through the three-way valve (9) back into the reservoir. The conversion was monitored from the reservoir by means of gas chromatography (A). The reaction was interrupted after the complete decomposition of the formaldehyde. The results shown in Table 1 were obtained:

Table 1

Conversion values and selectivity values of formaldehyde to 1-octene in the temperature range from 245-255 °C (Example 5, all data as % by weight)

Molar ratio of formaldehyde/1-octene	Exp. conversion of 1-octene	Yield of: 3-nonen-1-ol (selectivity ^[1])	Total yield ^[3]	[4]	Selectivity ^[2] of consumption of formaldehyde
4 : 100	3 %	3.0 % (99 %)	3.0 % (99 %)	>98 / 2	> 88 %
6 : 100	5 %	5.0 % (98 %)	5.1 % (99 %)	98 / 2	> 85 %
10 : 100	8 %	7.6 % (95 %)	7.8 % (98 %)	97 / 3	> 80 %
13 : 100	10 %	9.2 % (92 %)	9.5 % (95 %)	97 / 4	> 74 %
20 : 100	12 %	10.8 % (90 %)	11.3 % (94 %)	95 / 5	> 60 %
30 : 100	15 %	12.0 % (80 %)	13.1 % (87 %)	91 / 9	> 45 %

[1] Selectivity of formation of 3-nonen-1-ol related to conversion of 1-octene

[2] Selectivity related to the primary formation of the homoallyl alcohol

[3] Yield of 3-nonen-1-ol and its formate ester; indicated in brackets are the corresponding overall selectivity values related to the conversion to 1-octene

[4] Ratio of 3-nonen-1-ol to its formate esters

Example 6

Thermal addition of formaldehyde to 1-octene

1-octene was pumped by a high-pressure pump (1) from a reservoir (11) with gradation through the steel capillaries (4) located in the furnace, and with their temperatures adjusted as a result. By means of the needle valve (7) a pressure of 23 to 35 bar was set at the output of the steel capillaries. The delivery capacity of the pump was 0.2 to 3 ml/min. In the temperature-controlled decomposition apparatus (3), paraformaldehyde dried by P_2O_5 was presented. The steel capillaries were brought to a temperature of between 245 and 255 °C. Once the temperature had been reached, the decomposition apparatus was continuously heated from 140 to 230 °C. The monomer formaldehyde continuously discharged from the decomposition apparatus was carried by the fluid flow of 1-octene into the steel capillaries. The flow speed was adjusted in accordance with the decomposition temperature in the decomposition apparatus and the reaction temperature in the capillaries, in such a way that no more formaldehyde could be demonstrated at the outlet of the steel capillaries by means of the sampling valve (8). The reaction solution discharged passed, after cooling (5), through the three-way valve (9) back into the distillation apparatus (10). The 1-octene recovered at the head of the column was conducted back continuously into the reservoir. The conversion was monitored at the reactor outlet by means of gas chromatography, via the sampling valve (8). The products were continuously removed from the distillation (C). The reaction was interrupted after the complete decomposition of the formaldehyde. The results shown in Table 2 were obtained:

Table 2

Conversion values and selectivity values of formaldehyde to 1-octene in the temperature range from 245-255 °C (Example 6)

Molar ratio of formaldehyde/ 1-octene	Exp. conversion of 1-octene	Yield of: 3-nonen-1-ol (selectivity ^[1])	Total yield ^[3]	[4]	Selectivity ^[2] of consumption of formaldehyde
50 : 100	44 %	40.4 % (92 %)	42.1 % (95 %)	96 / 4	84 %
90 : 100	75 %	64.2 % (86 %)	71.8 % (96 %)	90 / 10	80 %

[1] Selectivity of formation of 3-nonen-1-ol related to conversion of 1-octene

[2] Selectivity related to the primary formation of the homoallyl alcohol

[3] Yield of 3-nonen-1-ol and its formate ester; indicated in brackets are the corresponding overall selectivity values related to the conversion to 1-octene

[4] Ratio of 3-nonen-1-ol to its formate esters

Example 7

Thermal addition of formaldehyde to cyclohexene and 4-octene

Cyclohexene and 4-octene respectively were pumped by a high-pressure pump (1) from a reservoir (II) with gradation through the steel capillaries (4), of which the temperature was adjusted by a furnace. By means of the needle valve (7) a pressure of 23 to 35 bar (6) was set at the output of the steel capillaries with the use of 4-octene, and of 170 bar (6) with the use of cyclohexene. The delivery capacity of the pump was 0.2 to 3 ml/min. In the temperature-controlled decomposition apparatus (3), paraformaldehyde dried by P_2O_5 was presented. The steel capillaries were brought to a temperature of between 265 and 270 °C. Once the temperature had been reached, the decomposition apparatus was continuously heated from 20 to 62 °C. The volume of trioxane continuously discharged from the decomposition apparatus was converted in the capillary (4) into monomer formaldehyde. The flow speed was adjusted in accordance with the decomposition temperature in the decomposition apparatus and the reaction temperature in the capillaries, in such a way that no more formaldehyde could be demonstrated at the outlet of the steel capillaries by means of the sampling valve (8).

The reaction solution discharged passed, after cooling (5), through the three-way valve (9) back into the reservoir (A). The conversion was monitored from the reservoir by means of gas chromatography (A). The reaction was interrupted after the complete decomposition of the formaldehyde. 4-octene was converted in an analogous manner. The results shown in Table 3 were obtained:

Table 3

Conversion values and selectivity values from the addition of formaldehyde to cyclohexene, 4-octene in the temperature range from 245-255 °C (Example 7)

Molar ratio of formaldehyde/olefin	Exp. conversion of -olefin	Yield of: Homoallyl alcohol (selectivity ^[1])	Total yield ^[3]	[4]	Selectivity ^[2] of consumption of formaldehyde
10 : 100 ^[5]	7 %	6.7 % (96 %)	6.9 % (99 %)	97 / 3	69 %
10 : 100 ^[6]	8 %	7.1 % (89 %)	7.5 % (93 %)	95 / 5	75 %

- [1] *Selectivity of formation of the corresponding homoallyl alcohol related to conversion of the olefin*
- [2] *Selectivity related to the primary formation of the homoallyl alcohol*
- [3] *Yield of homoallyl alcohol and its formate ester; indicated in brackets are the*
5 *corresponding overall selectivity values related to the conversion to olefin*
- [4] *Ratio of the corresponding homoallyl alcohol to its formate esters*
- [5] *Cyclohexene*
- [6] *4-octene*

10 Example 8

Hydration of homoallyl alcohol

The product from Example 5, consisting of a mixture of 3-nonen-1-ol and its formic acid esters in a ratio of 91 : 9, was converted with aqueous KOH solution and heated under
15 reflow for 24 hours. The reaction solution was extracted several times with diethylether.

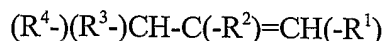
The combined extracts were dried by a molecular sieve and freed of diethylether by distillation. Weighing out and gas chromatographic monitoring of the product obtained showed that the formic acid ester was completely saponified to 3-nonen-1-ol.

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The 3-nonen-1-ol obtained in this way was dissolved in methanol, converted with palladium to activated carbon, and hydrated at 4 bar hydrogen pressure in a heated shaking apparatus. Once the hydrogen consumption had been completed, the substance was filtered from the catalytic converter. Gas chromatographic examination showed the
25 quantitative formation of 1-nonanol.

CLAIMS

1. A method for the manufacture of non-saturated homoallyl alcohols of the formula
- $$(R^4-)(R^3-)C=C(-R^2)-CH(CH_2OH)(-R^1)$$
- 5 and the formiates thereof, by conversion of formaldehyde with an olefin of the formula



or a mixture thereof,

whereby R^1 , R^2 , R^3 and R^4 independently of one another are hydrogen or a hydrocarbon residue with 1 to 26 carbon atoms, which optionally can be functionalised and/or two or more residues can be part of one or more cyclic rings,

essentially in the absence of water, whereby the method comprises the steps:

- 15 (A) preparing of monomeric formaldehyde containing a water content of less than 1.5 % by weight, obtainable by the drying of formaldehyde and/or a formaldehyde-precursor compound if the limiting value of 1.5 % by weight of water in the formaldehyde is exceeded,
 - (B) contacting the monomeric formaldehyde with the olefin or olefin mixture,
 - 20 (C) reacting the formaldehyde with the olefin at temperatures of from 200 to 300 °C and pressures of from 5 to 80 bar in one or more reactors, and
 - (D) separating the non-converted olefin and feeding the non-converted olefin back into the reactor/reactors.
2. The method according to claim 1, whereby formaldehyde and olefin are converted
- 25 in a flow tube reactor.
3. The method according to one of the preceding claims, characterised in that the monomeric formaldehyde is obtained by the decomposition of trioxane, paraformaldehyde, or methanol, preferably methanol and/or paraformaldehyde,
- 30 immediately before the conversion to homoallyl alcohol, and whereby, further preferred the formaldehyde and/or the formaldehyde-precursor compound is dried, preferably by means of chemical or physical drying means.
4. The method according to one of the preceding claims, characterised in that the
- 35 contacting of the monomeric formaldehyde with the olefin is effected by condensing and/or dissolving the monomeric formaldehyde into the olefin under pressures from 5 to 80 bar.



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5. The method according to one of the preceding claims, characterised in that the contacting of the monomeric formaldehyde with the olefin is effected at a higher pressure than step (C).
 6. The method according to one of the preceding claims, characterised in that the contacting of the monomer formaldehyde with the olefin takes place immediately before the reactor intake or in the front part of the reactor.
 7. The method according to one of the preceding claims, characterised in that the olefins are selected from the group of 1-olefins, 1,2-disubstituted olefins, and 1,1-disubstituted olefins, which in the allyl position carry a hydrogen atom and/or mixtures thereof.
 8. The method according to one of claims 1 to 6, characterised in that the olefins are selected from the group of non-saturated fatty acid esters.
 9. The method according to one of the preceding claims, characterised in that the molar ratio of formaldehyde to olefin is from 0.01 : 1 to 0.5 : 1, in particular from 0.03 : 1 to 0.3 : 1.
 10. The method according to one of the preceding claims, characterised in that the olefin comprises at least 4 carbon atoms, and preferably 5 to 22 carbon atoms.
 11. The method according to one of the preceding claims, characterised in that the reaction is carried out at a pressure, so that in the reaction chamber the formaldehyde and the olefin are of the same phase and preferably are both present in the fluid phase.
 12. The method according to one of the preceding claims, characterised in that the separation of the non-converted olefin is effected by one or more distillations.
 13. The method according to one of claims 1 to 11, characterised in that the separation of the non-converted olefin is effected by adsorption.
 14. The method according to one of the preceding claims, characterised in that after purification and enrichment the non-converted olefin from the product stream is



fed back into the reactor in whole or in part.

15. The method according to one of the preceding claims, characterised in that the conversion takes place in the absence of solvents, promoters, bases, and/or catalysts.

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16. The method according to one of the preceding claims, characterised in that the reaction parameters are adjusted in such manner that between 1 % and 15 % of the olefin is converted per reactor pass.

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Fig. 1/2

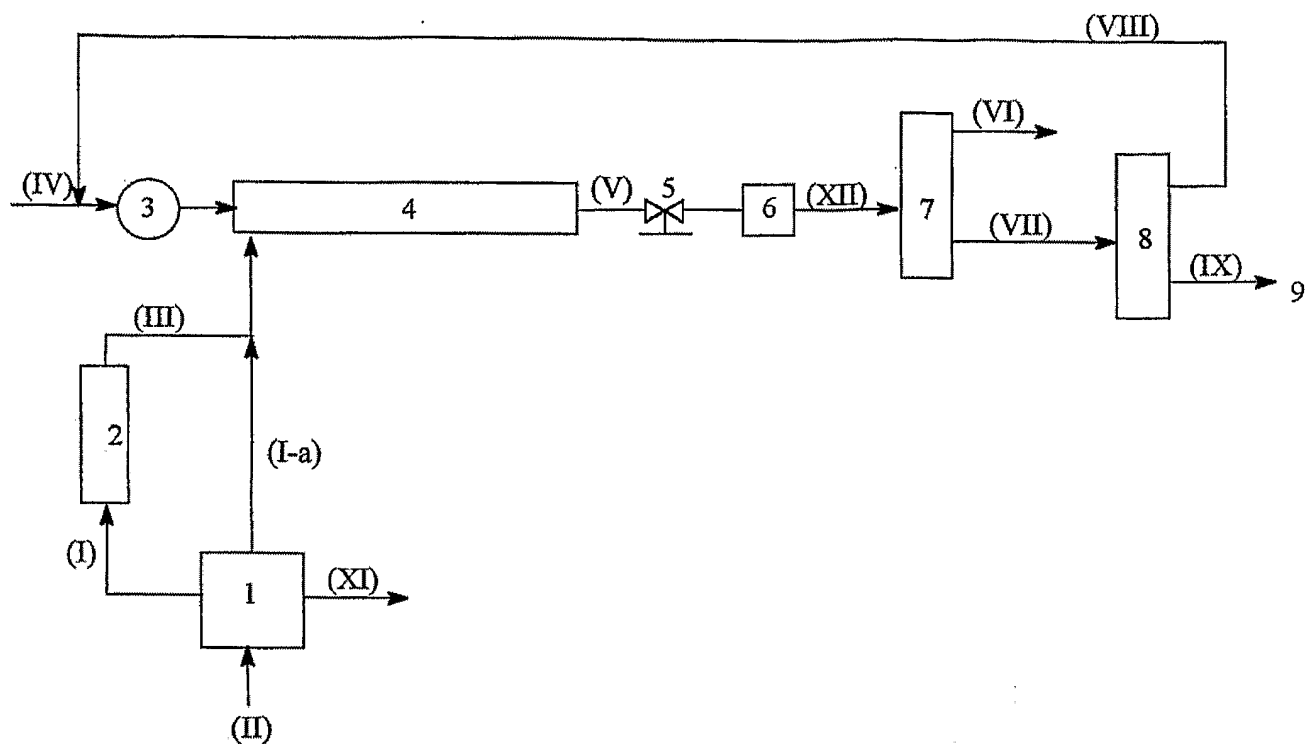
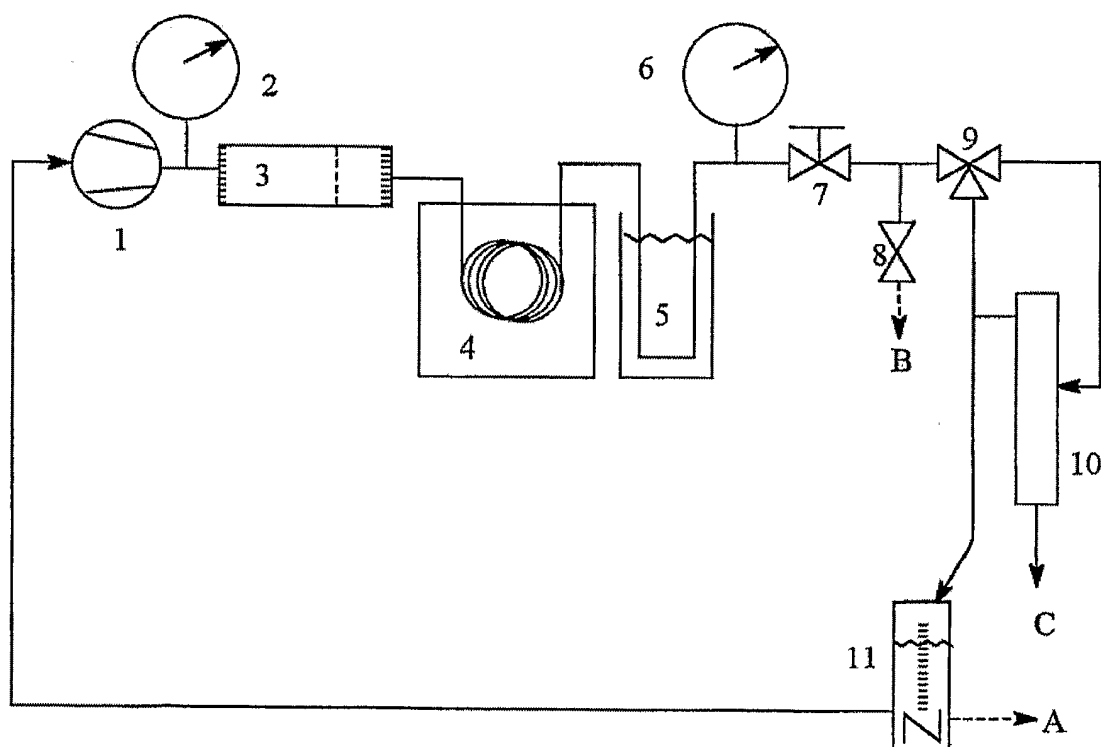


Fig. 2/2



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/14939

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C29/38 C07C33/03 C07C47/045 C07C45/55 C07C45/60
C07C45/00 C07C47/04 C07C69/07

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB 1 438 011 A (JEFFERSON CHEM CO INC) 3 June 1976 (1976-06-03) examples 1-5 -----	1
A	GB 1 197 971 A (THE BRITISH PETROLEUM COMPANY LTD) 8 July 1970 (1970-07-08) claims -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

16 April 2004

Date of mailing of the international search report

28/04/2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/14939

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