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(54) **PROCEDE DE PRODUCTION D'ACETALS**

(54) **METHOD FOR PRODUCING ACETALS**

(57) L'invention concerne un procédé de production d'acétals par réaction d'éthers d'allyle avec des alcools, procédé dans lequel on fait réagir un éther d'allyle avec un alcool en phase liquide en présence d'un catalyseur homogène constitué d'un composé organométallique d'un élément du groupe VIA et/ou VIIIA de la classification périodique des éléments ou en présence d'un catalyseur hétérogène contenant un ou plusieurs éléments des groupes IA, VIA, VIIA et/ou VIIIA de la classification périodique des éléments, et ce, dans un environnement essentiellement exempt d'eau.

(57) The invention relates to a method for producing acetals by reacting allyl ethers with alcohols. According to said method, an allyl ether is reacted with an alcohol in liquid phase in the presence of a homogenous catalyst from an organometallic compound of an element from group VIA and/or VIIIA of the periodic table of elements or in the presence of a heterogeneous catalyst containing one or more elements from the groups IA, VIA, VIIA and/or VIIIA of the periodic table of elements in essentially water-free conditions.

PCT

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(54) Title: METHOD FOR PRODUCING ACETALS

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON ACETALEN

(57) Abstract

The invention relates to a method for producing acetals by reacting allyl ethers with alcohols. According to said method, an allyl ether is reacted with an alcohol in liquid phase in the presence of a homogenous catalyst from an organometallic compound of an element from group VIA and/or VIIIA of the periodic table of elements or in the presence of a heterogeneous catalyst containing one or more elements from the groups IA, VIA, VIIA and/or VIIIA of the periodic table of elements in essentially water–free conditions.

(57) Zusammenfassung

Verfahren zur Herstellung von Acetalen durch die Umsetzung von Allylethern mit Alkoholen, in dem man einen Allylether mit einem Alkohol in flüssiger Phase in Gegenwart eines homogenen Katalysators aus einer Organometallverbindung eines Elementes aus der Gruppe VIA und/oder VIIIA des Periodensystems der Elemente oder in Gegenwart eines heterogenen Katalysators, der ein oder mehrere Elemente aus den Gruppen IA, VIA, VIIA und/oder VIIIA des Periodensystems der Elemente enthält, unter im wesentlichen wasserfreien Bedingungen umsetzt.

METHOD FOR PRODUCING ACETALS

The present invention relates to a process for the preparation of acetals by reacting an allyl ether with an alcohol.

Acetals are widely used in industry, for example as starting materials for the preparation of the corresponding aldehydes by hydrolysis of the acetal or as reagents for preparing acetals from aldehydes or ketones by transacetalation. In perfumery, acetals are used as fragrances [cf. Riechstoffe, Aromen, Kosmetika 27 (1977), 71].

Acetals are prepared in general from the corresponding aldehydes or ketones by reaction with an alcohol under acid catalysis [Riechstoffe, Aromen, Kosmetika 27 (1977), 71]. In many cases, the relevant aldehydes are not available in the desired amounts from natural sources or the price of the aldehydes obtainable from natural raw materials is so high that it prevents extensive industrial use of these aldehydes for the various purposes. There is therefore a need for processes which permit the economical preparation of acetals from petrochemical raw materials.

US-A 4 788 325 and Chang [J. Organomet. Chem. 492 (1995) 31] describe the reaction of allyl ethers with alcohols in the presence of hydrogen and carbon monoxide using dicobaltoctacarbonyl ($Co_2(CO)_8$) as a catalyst. This is either used directly in the reaction as a catalyst or is produced in situ in the reaction mixture by carbonylation of cobalt salts with carbon monoxide under high pressure. Under reaction conditions, the dicobaltoctacarbonyl is converted by the hydrogen into hydridocobalttetracarbonyl ($HCo(CO)_4$), which is the actual catalytically active species. The disadvantage of this process is that the cobalt carbonyl compounds used are relatively readily volatile and are partly discharged with the acetal when the product mixture is worked up by distillation, so that, before being further used, for example as a fragrance, said acetal must be freed, in an expensive cobalt-removal stage, from cobalt carbonyls contained therein. This process is therefore uneconomical.

US-A 4 658 069 relates to a process for converting allyl ethers, which additionally contain a formyl or carboxyl group, into the corresponding diacetals, in a first stage the allyl ether being reacted with an alkanol under anhydrous conditions and the water

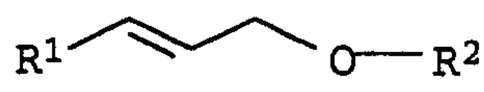
formed in this reaction then being removed and, in a second stage, the allyl ether acetal obtained in the first stage being converted into the saturated diacetal with the aid of a ruthenium halide catalyst and an alkanol. Other suitable catalysts are iridium, rhodium, osmium, palladium and platinum halides. Since these halides of platinum metals are not sufficiently stable under the reaction conditions and tend to deposit the relevant platinum metal on the walls of the reaction apparatus, leading to losses of the expensive platinum metal, this process is uneconomical on an industrial scale.

JP-A 25114/1972 relates to a process for the preparation of acetals from allyl ethers by reacting them with an alkanol in the presence of a ruthenium(III) chloride catalyst. In the example of this application, 1-methoxy-2,7-octadiene is reacted with methanol and by means of $RuCl_3$ under a nitrogen atmosphere to give 1,1-dimethoxyoct-7-ene. This process, too, has the disadvantage of poor catalyst stability.

It is an object of the present invention to provide an economical process for the preparation of acetals from allyl ethers which does not have the disadvantages of the prior art.

We have found that this object is achieved by a process for the preparation of acetals by reacting allyl ethers with alcohols, wherein an allyl ether is reacted with an alcohol in the liquid phase in the presence of a homogeneous catalyst comprising an organometallic compound of an element of group VIA and/or VIIIA of the Periodic Table of Elements or in the presence of a heterogeneous catalyst which contains one or more elements of the groups VIA, VIIA and/or VIIIA of the Periodic Table of Elements, under essentially anhydrous conditions.

The starting materials used in the novel process are allyl ethers of the formula I



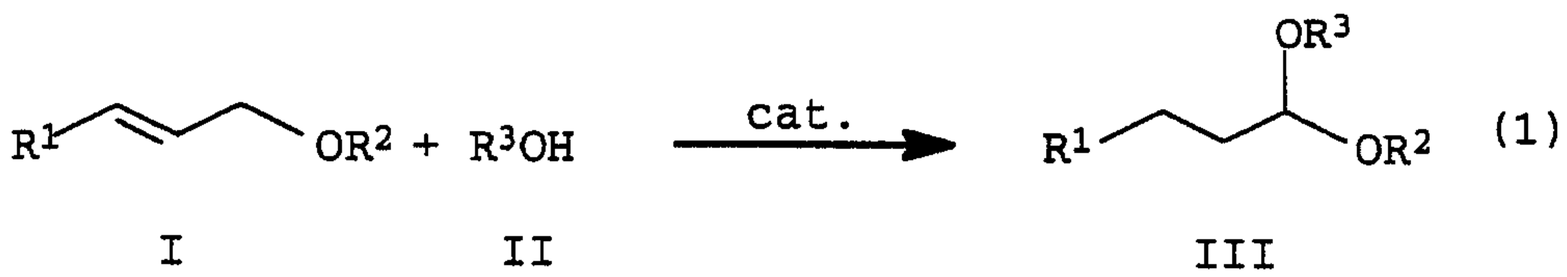
I

where R^1 is hydrogen or an organic radical, in particular a cyclic, straight-chain or branched hydrocarbon group of 1 to 17, preferably 1 to 10, carbon atoms. Examples of such hydrocarbon groups are alkyl, C_3-C_{17}-alkenyl whose double bond is preferably not conjugated with the allylic double bond, aryl, such as phenyl

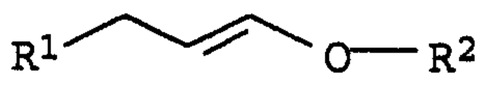
or naphthyl, C_3-C_8-cycloalkyl, alkylaryl and aralkyl. Depending on their size, these hydrocarbon groups may be substituted by 1 to 3 substituents which are inert under the reaction conditions, such as ester groups or alkoxy or aryloxy groups. R^1 is preferably straight-chain, branched or cyclic alkyl. R^2 in the allyl ether of the formula I is an organic radical having 1 to 20, preferably 1 to 10, carbon atoms. R^2 is preferably a hydrocarbon group, for example straight-chain or branched C_1-C_{20}-alkyl, preferably C_1-C_{10}-alkyl, C_3-C_8-cycloalkyl, C_3-C_{20}-alkenyl, preferably C_3-C_{12}-alkenyl, or C_5-C_8-cycloalkenyl, where the double bond of this alkenyl group is preferably not present α to the oxygen atom of the allyl ether, C_6-C_{10}-aryl, such as phenyl or naphthyl, or C_7-C_{11}-aralkyl or alkylaryl. R^2 is preferably bonded to the oxygen atom of the allyl ether I via a primary or secondary carbon atom. R^2 is particularly preferably straight-chain or branched alkyl or alkenyl. Depending on their size, the organic radicals R^2 may carry 1 or 2 substituents which are inert under the reaction conditions, for example C_1-C_{10}-alkoxy. Depending on its size, R^2 may also be substituted by 1 or 2 hydroxyl groups. However, R^2 preferably carries no further substituents.

Some allyl ethers I which are suitable as starting materials in the novel process are listed below by way of example, merely for explanatory purposes: allyl methyl ether, allyl ethyl ether, allyl n-propyl ether, allyl n-butyl ether, diallyl ether, (but-2-enyl) methyl ether, (but-2-enyl) ethyl ether, (but-2-enyl) n-propyl ether, (but-2-enyl) n-butyl ether, di(but-2-enyl) ether, octa-2,7-dienyl methyl ether, octa-2,7-dienyl n-butyl ether, di(octa-2,7-dienyl) ether and 1-butoxydodeca-2,7,11-triene.

In the alcohol R^3OH II, which is used in the novel process for producing the acetals III according to equation (I)



where this reaction presumably takes place via the isomerization of the allyl ether I to an enol ether intermediate IV



IV

radical R^3 may be identical to or different from the radical R^2 contained in the allyl ether used. Preferably primary or secondary, particularly preferably primary, alcohols R^3OH are used in the novel process. Tertiary alcohols R^3OH may also be used, but steric hindrance may occur in the course of the reaction, depending on the bulkiness of the radical R^2. The alcohol R^3OH is therefore preferably chosen so that no steric hindrance by the radical R^2 occurs. Aliphatic C_1-C_4-alcohols are particularly preferably used as R^3OH, in particular methanol, ethanol, n-propanol, isobutanol and n-butanol. The alcohols R^3OH used can of course also be polyhydric alcohols, such as ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol or 1,6-hexanediol. If R^2 contains a free hydroxyl group, this may undergo an intramolecular or an intermolecular reaction with the double bond with formation of cyclic or acyclic acetals, ie. in such a case the hydroxyl group present in the radical R^2 acts as alcohol R^3OH.

A large number of organometallic compounds of transition metal elements, in particular those containing elements of groups VIA and VIIIA of the Periodic Table of Elements, preferably molybdenum, iron, cobalt, nickel, in particular the platinum metals ruthenium, rhodium, palladium, platinum, osmium and/or iridium, particularly preferably ruthenium, rhodium, iridium or osmium, may be used in the novel process as homogeneous catalysts for acetalating the allyl ether I to give the acetal III. For the purposes of the present application, organometallic compounds are understood as meaning complexes of the stated transition metals with organic ligands which contain hetero atoms such as phosphorus, antimony, arsenic, nitrogen, sulfur and/or oxygen, and are coordinated via free electron pairs with the transition metal, for example organic amine ligands, organic phosphine ligands, chelate ligands, such as acetylacetone and dioximes, such as dimethyl dioxime, furil dioxime or benzil dioxime, ureas or thioureas, 8-hydroxyquinoline, monodentate or polydentate, in particular bidentate organophosphine and organophosphite ligands, organoarsine and organostibine ligands, and aromatic, nitrogen-containing ligands for whose property as a complexing agent the (-N=C-C=N-) structural unit is responsible, for example 2,2'-bipyridine or 1,10-phenanthroline, and the ligands derived from these parent substances by substitution, for example terpyridines. These complexes may be present as neutral complexes or may be charged and may form a salt with an anion. On the other hand, simple salts of these transition metals with, for example, carboxylic acid, carbonic acid or hydrocyanic acid, which contain none of the abovementioned organic ligands, are not considered as organometallic compounds for the purposes of the present

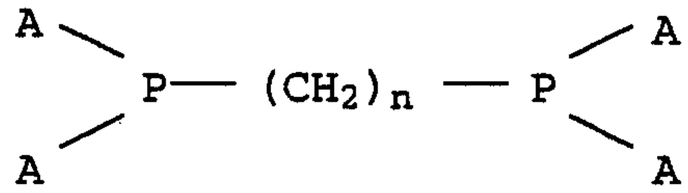
application. The same applies to carboxylato, cyano or carbonyl complexes of the transition metals, such as dicobaltoctacarbonyl ($Co_2(CO)_8$) or hydridocobalttetracarbonyl ($HCo(CO)_4$), which contain none of the abovementioned organic ligands. On the other hand, complexes of the transition metals with the abovementioned organic ligands which additionally contain carboxylates, alcoholate, cyanide, carbonate or the carbonyl ligands bonded in complex form, or which contain a carboxylate, alcoholate, cyanide, carbonate or sulfonate anion as an anion for the positively charged organometallic complex of the transition metal are understood as being covered by the definition of organometallic compounds.

The ligands used may be either monodentate or polydentate, for example bidentate phosphine ligands. Suitable phosphine ligands are, for example, trialkylphosphines, triarylphosphines, alkyldiarylphosphines, aryldialkylphosphines, aryldiphosphines, alkyldiphosphines and arylalkyldiphosphines. The alkyl-carrying phosphine ligands may contain identical or different C_1-C_{20}-alkyl, preferably C_1-C_6-alkyl, or cycloalkyl groups. The aryl-carrying phosphine ligands may contain identical or different C_6-C_{12}-aryl, in particular phenyl or naphthyl, as well as diphenyl groups. Other phosphine ligands which may be used for complexing the group VIA or VIIIA elements are those which carry heterocycloaliphatic groups, such as pyrrolidine, imidazolidine, piperidine, morpholine, oxazolidine, piperazine or triazolidine groups, or heteroaromatic groups, such as pyrrole, 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 ligands may be unsubstituted or may carry substituents which are inert under the reaction conditions, such as C_1-C_4-alkoxy or di-C_1-C_4-alkylamino, C_1-C_6-alkyl, nitro, cyano or sulfonate groups. Examples of suitable sulfonated phosphine ligands are in particular triphenylphosphinetrisulfonate (TPPTS) and triphenylphosphinemonosulfonate (TPPMS) (Angew. Chem. 105 (1993), 1588).

There is in principle no restriction to the applicability of such ligands for complexing the group VIA or VIIIA elements in the novel process. For cost reasons, however, ligands which can be prepared in a simple manner are preferably used.

A list of such ligands which serves merely by way of example is the following: trimethylphosphine, triethylphosphine, tripropylphosphine, triisopropylphosphine, tributylphosphine,

trioctylphosphine, tridecylphosphine, tricyclopentylphosphine, tricyclohexylphosphine, triphenylphosphine, tritolylphosphine, cyclohexyldiphenylphosphine, tetraphenyldiphosphinomethane, 1,2-bis(diphenylphosphino)ethane, tetramethyldiphosphino methane, tetraethyldiphosphino methane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, tetra-tert-butyldiphosphinomethane, 1,2-bis(dimethylphosphino)ethane, 1,2-bis(diethylphosphino)ethane, 1,2-bis(dipropylphosphino)ethane, 1,2-bis(diisopropylphosphino)ethane, 1,2-bis(dibutylphosphino)ethane, 1,2-bis(di-t-butylphosphino)ethane, 1,1-bis(dicyclohexylphosphino)methane, 1,2-bis(dicyclohexylphosphino)ethane, 1,4-bis(dicyclohexylphosphino)butane and the bisphosphine ligands described in EP-A 279 018, EP-A 311 619, WO 90/06810 and EP-A 71 281. Preferred phosphine ligands in addition to triphenylphosphine (abbreviated to PPh_3) are bidentate phosphine ligands bridged via C_1-C_4-alkylene groups and of the general formula



where n is an integer from 1 to 4 and the radicals A are identical or different C_1-C_{10}-alkyl or C_5- or C_6-cycloalkyl groups, some typical examples of which were mentioned above.

In addition to being prepared by the processes described in the abovementioned patent applications, the alkyl- or arylphosphine ligands can be prepared by methods known per se, for example by the processes stated in Houben-Weyl, Methoden der Organischen Chemie, Volume XII/1, 4th edition, pages 17-65 and pages 182-186, Thieme, Stuttgart, 1963, and Volume E 1, 4th edition, pages 106-199, Thieme, Stuttgart, 1982.

Suitable phosphite ligands are, for example, trialkyl phosphites, alkyl diaryl phosphites, triaryl phosphites, alkyl bisphosphites, aryl bisphosphites and alkyl aryl bisphosphites. The alkyl-carrying phosphite ligands may contain identical or different C_1-C_{10}-alkyl, preferably C_1-C_6-alkyl, or cycloalkyl groups. The aryl-carrying phosphite ligands may contain identical or different C_6-C_{12}-aryl, in particular phenyl or naphthyl, groups

as well as the diphenyl group or the binaphthyl group. Other phosphite ligands which may be used for complexing the transition metals are those which carry heterocycloaliphatic groups, such as pyrrolidine, imidazolidine, piperidine, morpholine, oxazolidine, piperazine or triazolidine groups, or heteroaromatic groups, such as pyrrole, imidazole, oxazole, indole, pyridine, quinoline, pyrimidine, pyrazole, pyrazine, pyridazine or quinoxazoline groups, together with other alkyl or aryl groups. The alkyl or aryl groups of the phosphite ligands may be unsubstituted or may carry substituents which are inert under the reaction conditions, such as C_1-C_4-alkoxy, di-C_1-C_4-alkylamino, C_1-C_6-alkyl, hydroxyl, nitro, cyano or sulfonate groups. The sulfonate-substituted phosphite ligands and their complexes are in general water-soluble. Suitable phosphite ligands are, for example, trimethyl phosphite, triethyl phosphite, tripropyl phosphite, triisopropyl phosphite, tributyl phosphite, tricyclopentyl phosphite, tricyclohexyl phosphite, triphenyl phosphite and the mono- and bisphosphite ligands described in EP-A 472 071, EP-A 213 639, EP-A 214 622, DE-A 2 733 796, EP-A 2261, EP-A 2821, EP-A 9115, 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 addition to phosphine or phosphite ligands, 2,2'-bipyridine or 1,10-phenanthroline ligands of the alkyl- or aryl-substituted or fused 2,2'-bipyridine or 1,10-phenanthroline derivatives which contain the (-N=C-C=N-) group responsible for the complex-forming property of the 2,2'-bipyridine or 1,10-phenanthroline ligands, for example 2,2'-biquinoline, 4,7-diphenyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 4,5-diazafluorene, dipyrido[3,2-a:2',3'-c]phenazine, 2,2',6',2''-terpyridine, etc., may also be used in the novel process. Some of these ligands are commercially available, for example 2,2'-bipyridine or 1,10-phenanthroline, and others can be prepared by the methods stated in Synthesis 1 (1976) or Aust. J. Chem. 23 (1970), 1023.

Those complexes of the elements of Group VIA or VIIIA which may be used in the novel process may be either produced in situ in the reaction mixture or formed beforehand and then added to the reaction mixture. For the in situ production of these complexes, in general compounds of group VIA or VIIIA elements, for example their halides, preferably their chlorides, bromides or iodides, the nitrates, cyanides or sulfates or, particularly preferably complex compounds of these metals, such as acetylacetonates, carboxylates, carbonyl complexes or olefin complexes, such as ethene or butadiene complexes, are fed to the reaction mixture together with the relevant ligands, whereupon the complexes which may be used according to the invention form in the reaction

mixture. In general, the relevant ligand is added here in a molar ratio of from 1 to 200, preferably from 1 to 50, in particular from 1 to 10, based on the group VIA or VIIIA element.

Among the abovementioned organometallic compounds of the transition metals, platinum metal carbonyl complexes containing phosphorus-containing ligands, in particular phosphine ligands, such as $HRh(PPh_3)_3(CO)$, $IrCl(CO)(PPh_3)_3$, $[Ir(cyclooctadienyl)PPh_3)_2]PF_6$, $HRuCl(PPh_3)_3(CO)$, $HRu(CO)(CH_3COO)(PPh_3)_2$, $H_2Ru(CO)(PPh_3)_3$, $HRuCl(CO)$(Hexyldiphenylphosphine)$_3$, $RuH_2(PPH_3)_4$, $RuCl_2(CO)_2(PPh_3)_3$ or $RuH(CO)(C_9H_{19}COO)(PPh_3)_2$, where $C_9H_{19}COO$ is the capric acid anion, are especially preferred as homogeneous catalysts in the novel process. Among these homogeneous catalysts in turn, the halogen-free complexes are preferred, for example those which contain, as ligands, the conjugated base of an O-H-acidic, organic compound, O-H-acidic, organic compounds being understood as meaning those compounds which are acidic in aqueous solution, such as monocarboxylic acids, monosulfonic acids or non-chelating phenols. C_2-C_{20}-carbonic acid anions which preferably originate from a monocarboxylic acid, such as acetate, propionate, butyrate, isobutyrate, valerate, pivalate, caproate, enanthate, caprylate, 2-ethylhexanoate, 2-propylheptanoate, caprate, laurate, myristate, palmitate, stearate, oleate, benzoate, alkylbenzoate, naphthoate and alkylnaphthoate anions, or non-chelating phenolate anions or sulfonate anions, may advantageously serve as such ligands.

Phenolates which can advantageously be used as ligands in such organic transition metal compounds are, for example, the phenolate and naphtholate anions and phenolate and naphtholate anions substituted on the aromatic nucleus by substituents which are inert under the reaction conditions, for example C_1-C_{20}-alkyl-substituted, preferably C_1-C_{10}-alkyl-substituted, phenolates or naphtholates, such as methylphenolate, nonylphenolate, 2,6-di-tert-butylphenolate or 2,6-di-tert-butyl-4-methylphenolate anions.

Sulfonate ligands which can advantageously be used for this purpose are, for example, alkanesulfonates, such as the methanesulfonate, octanesulfonate, dodecanesulfonate, octadecanesulfonate or trifluoromethanesulfonate anion, or arylsulfonates, such as the toluenesulfonate anion.

The preparation of the homogeneous catalysts which contain ligands originating from acidic organic compounds and can be used according to the invention is outlined briefly below for the abovementioned ruthenium complex compounds as a typical example of similar complex compounds of other transition metals:

These complexes containing carboxylate ligands can be prepared, for example starting from $RuH_2(PPh_3)_3(CO)$, which is obtainable, for example, according to Uttley et al., Inorganic Syntheses, Vol. XVII (1977), 125, by reaction with the corresponding carboxylic acids similarly to the methods developed by Robinson et al., J. Chem. Soc., Dalton Trans. (1973), 1912, Frediani et al., ibid. (1990) 165, ib. (1990) 1705, ib. (1990) 3663 and Frediani et al., J. Organomet Chem. 454, C17-C19 (1993). The corresponding complexes containing phenolate ligands can be obtained in a similar manner by reacting $H_2Ru(CO)(PPh_3)_3$ with the relevant phenols. Complexes containing sulfonate ligands are obtainable, for example, by the process described in US-A 4 892 955. The halogen-containing homogeneous catalysts can be prepared, for example, by the processes of Uttley et al., Inorganic Syntheses, Vol. XV, (1974), 45, by reacting $RuCl_3$ with formaldehyde.

The abovementioned catalysts can be added as such to the reaction batch or - this applies in particular to homogeneous catalysts containing carboxylate or phenolate ligands - produced in situ in the reaction mixture by reacting $RuH_2(PPh_3)_3(CO)$ with the relevant carboxylic acid or the relevant phenol.

Furthermore, starting from complexes which have no hydrido or carbonyl ligands, complexes containing hydrido and/or carbonyl ligands can be generated in situ in the reaction mixture by forcing in molecular hydrogen and/or carbon monoxide.

Such organic transition metal compounds modified with carboxylate, sulfonate or phenolate ligands and additionally containing phosphorus-containing ligands, in particular phosphine or phosphite ligands, preferably phosphine ligands and, if desired, carbonyl ligands, in particular organic ruthenium compounds, are distinguished in the novel process as homogeneous catalysts for catalysis of the acetalation by high activity and selectivity as well as by high stability and hence a long time on stream.

The advantageous properties of these homogeneous catalysts can additionally be improved by carrying out the acetalation in the presence of an amount of the relevant acidic compound which is greater than the stoichiometric amount required for the formation of the relevant transition metal carboxylate or phenolate complex, so that, in the reaction mixture, the relevant acidic compound in free form is in equilibrium with the organic transition metal compound serving as the homogeneous catalyst. For this purpose, the acidic compound used is advantageously the same as that bonded to the transition metal in the organic transition metal compound, but the addition of other acidic organic compounds is equivalent to this measure. In such a procedure, the acidic organic compound is generally used in a molar ratio of 1:1, based on the organic transition metal compound acting as the homogeneous catalyst.

Although for the acetalation reaction it is not necessary to add hydrogen to the reaction mixture, the addition of small amounts of hydrogen, if necessary together with the addition of small amounts of carbon monoxide when carbonyl-containing homogeneous catalysts are used, can lead to a prolongation of the time on stream of these homogeneous catalysts. In practice, synthesis gas can be used for this purpose. It should be noted here that, depending on the reaction temperature used and partial pressure employed, the hydrogen and/or the carbon monoxide react with the transition metal complexes present as homogeneous catalysts in the reaction mixture, as a result of which a plurality of catalytically active, organometallic transition metal complexes, which differ essentially in the number of their hydrido and carbonyl ligands, may be present in equilibrium with one another in the reaction mixture under these conditions.

To improve the activity, selectivity and stability of the homogeneous catalysts, in particular of the homogeneous catalysts containing phosphorus-containing ligands, the phosphine or phosphite is generally added in from 2 to 100, preferably from 2 to 20, particularly preferably from 2 to 10, times the molar amount, based on the phosphine or phosphite complex of the transition metal. If the transition metal complex serving as the homogeneous catalyst is produced in situ in the reaction mixture, a correspondingly large excess of phosphine or phosphite ligand, based on the relevant transition metal, is advantageously added.

The transition metal catalysts which are homogeneously soluble in the reaction medium are generally used in amounts of from 0.001 to 1, preferably from 0.01 to 1, mol%, based on the allyl ether I

fed to the reactor. It is self-evident to a person skilled in the art that the amount of homogeneous catalyst to be added is dependent on the catalyst activity of the homogeneous catalyst used in each case. Depending on the type of homogeneous catalyst used, a larger or smaller amount of catalyst may therefore also advantageously be added to the reaction mixture. The optimum amount for the homogeneous catalyst used in each case is advantageously determined in a preliminary experiment.

The acetalation with the aid of the stated homogeneous catalysts can be carried out batchwise, for example in stirred kettles, or continuously, for example in loop reactors or stirred kettle cascades, at in general from 20 to 200°C, preferably from 60 to 180°C, in particular from 80 to 160°C, and at in general from 1 to 100, preferably from 1 to 60, bar. The acetalation can be effected in the presence or absence of added solvents, such as aliphatic or aromatic hydrocarbons, eg. toluene, benzene or cyclohexane, ethers, eg. dibutyl ether, tetrahydrofuran or dioxane, or liquid, low molecular weight polyalkylene glycols, halogenated aliphatic or aromatic hydrocarbons, eg. chloroform, dichloromethane, chlorobenzene or dichlorobenzene, sulfoxides or sulfones, eg. dimethyl sulfoxide or sulfolane.

The novel acetalation is carried out under essentially anhydrous conditions, ie. in the absence of technically effective amounts of water, since the presence of water has an adverse effect on the result of the acetalation reaction. It is self-evident that the presence of traces of water which have no measurable effect on yield and cost-efficiency of the novel process can be tolerated.

Instead of being carried out in these conventional solvents, the isomerization and acetalation of the allyl ether I to give the acetal III can also be effected in a phosphine melt. This procedure can advantageously be used in the case of phosphine-containing homogeneous catalysts. In general, the phosphine serving virtually as the solvent can in principle be freely chosen, but the phosphine used in the melt is preferably that which serves as a ligand in the transition metal complex used as the homogeneous catalyst.

The addition of the alcohol R^3OH II can be varied within wide ranges. The equimolar amount required for the formation of the acetal III can, if desired, also be exceeded. In general, the alcohol R^3OH II is fed to the reactor in a molar ratio II/I of from 1 : 1 to 100 : 1, preferably from 1 : 1 to 10 : 1, in

particular from 1 : 1 to 5 : 1, based on the allyl ether I used. A larger molar excess, based on the allyl ether I, of the alcohol R^3OH II generally do not have an adverse effect on the result of the reaction, but the alcohol R^3OH II is advantageously used in the abovementioned ratios.

After the end of the reaction, the reaction product is generally worked up by distillation, and the homogeneous catalyst can be recovered from the bottom product of the distillation and, if desired, reused. If it is desired to reuse the catalyst, a solvent which has a higher boiling point than the acetal III formed in the reaction can advantageously be added to the reaction mixture before the distillation. If the homogeneous catalyst used is thermally and chemically stable under the conditions of the distillation, the addition of a high-boiling solvent can be dispensed with and the homogeneous catalyst can be recycled to the reaction, for example in a triphenylphosphine melt.

In a further embodiment of the novel process, the isomerization and acetalation of the allyl ether I to the acetal III is carried out using a heterogeneous catalyst, the process advantageously being carried out in the liquid phase.

It was found, surprisingly, that conventional heterogeneous hydrogenation catalysts which are essentially insoluble in the reaction medium can be used as catalysts for the conversion of the allyl ether I into the acetal III. Preferred among these hydrogenation catalysts are those which contain one or more elements of groups IA, VIA, VIIA or VIIIA, if required in combination with one or more elements of group VA, of the Periodic Table of Elements, in particular chromium, molybdenum, tungsten, rhenium, ruthenium, cobalt, nickel, rhodium, iridium, osmium, palladium and/or platinum, if required in combination with iron and/or copper.

In the novel process, for example, precipitated catalysts can be used as heterogeneous catalysts. Such catalysts can be prepared by precipitating their catalytically active components from their salt solutions, in particular from the solutions of their nitrates and/or acetates, for example by adding alkali metal and/or alkaline earth metal hydroxide and/or carbonate solutions, such as, for example, sparingly soluble hydroxides, hydrated oxides, basic salts or carbonates, then drying the precipitates obtained and then converting these, by calcination at in general from 300 to 700°C, in particular from 400 to 600°C, into the

relevant oxides, mixed oxides and/or mixed-valency oxides, which are reduced to the relevant metals and/or to oxidic compounds of low oxidation state, for example by treatment with reducing agents, such as hydrogen or hydrogen-containing gases, at, as a rule, from 50 to 700°C, in particular from 100 to 400°C, and are converted into the actual, catalytically active form. As a rule, the reduction is continued until no more water is formed. In the production of precipitated catalysts which contain a carrier, the precipitation of the catalytically active components may be effected in the presence of the relevant carrier. However, the catalytically active components may advantageously also be precipitated simultaneously with the carrier from the relevant salt solutions, as is the case, for example, in the precipitation of the catalytically active components by means of a waterglass solution.

Catalysts which contain the catalytically active metals or metal compounds deposited on a carrier are preferably used in the novel process. In addition to the abovementioned precipitated catalysts which also contain a carrier in addition to the catalytically active components, in general supported catalysts in which the catalytically active components have been applied to a carrier, for example by impregnation are suitable for the novel process.

The method of application of the catalytically active metals to the carrier is as a rule not critical for the result of the process and may be effected in a variety of ways. The catalytically active metals can be applied to these carriers, for example, by impregnation with solutions or suspensions of the salts or oxides of relevant elements, drying and subsequent reduction of the metal compounds to the relevant metal or oxidic compounds of low oxidation state by means of a reducing agent, preferably with the aid of hydrogen, hydrogen-containing gases or hydrazine. Another possibility for applying the catalytically active metals to these carriers is to impregnate the carriers with solutions of thermally readily decomposable salts, for example with nitrates, or with thermally readily decomposable complex compounds, for example carbonyl or hydrido complexes of the catalytically active metals, and to heat the carrier impregnated in this manner to 300 to 600°C for thermal decomposition of the adsorbed metal compounds. This thermal decomposition is preferably carried out under an inert gas atmosphere. Suitable inert gases are, for example, nitrogen, carbon dioxide, hydrogen or noble gases. Furthermore, the catalytically active metals may be deposited on the catalyst carrier by vapor deposition or by flame spraying.

The content of the catalytically active metals in these supported catalysts is in principle not critical for the success of the novel process. It is self-evident to a person skilled in the art that higher contents of catalytically active metals in these supported catalysts lead to higher space-time yields than lower contents. However, supported catalysts whose content of catalytically active metals is from 0.1 to 80, preferably from 0.5 to 30, % by weight, based on the total weight of catalyst, are generally used. Since these stated contents are based on the total catalyst, including carrier, but the different carriers have very different densities and specific surface areas, it is however also possible to use amounts less than or greater than the stated ones without adversely affecting the result of the novel process. It is of course also possible to apply a plurality of the catalytically active metals to the respective carriers. Furthermore, the catalytically active metals can be applied to the carrier, for example, by the processes of DE-A 2 519 817, EP-A 147 219 and EP-A 285 420. In the catalysts according to the abovementioned publications, the catalytically active metals are present as alloys which are produced by thermal treatment and/or reduction of the salts or complexes of the abovementioned metals, which salts or complexes are deposited on a carrier, for example, by impregnation.

In general, the oxides of aluminum or of titanium, zirconium dioxide, silica, kieselguhr, silica gel, aluminas, eg. montmorillonites, silicates, such as magnesium silicates or aluminum silicates, zeolites, such as ZSM-5 or ZSM-10 zeolites, and active carbon may be used as carriers. Preferred carriers are aluminum oxides, titanium dioxides, zirconium dioxide and active carbon. It is of course also possible to use mixtures of different carriers as the carrier for catalysts which may be used in the novel process.

Examples of heterogeneous catalysts for carrying out the acetalation are the following catalysts:

platinum dioxide, palladium on alumina, palladium on silica, palladium on barium sulfate, palladium on zirconium dioxide, rhodium on active carbon, rhodium on alumina, ruthenium on silica or active carbon, nickel on silica, cobalt on silica, cobalt on alumina, iron carbonyl powder, rhenium/palladium on active carbon, rhenium/platinum on active carbon, platinum oxide/rhodium oxide mixtures, platinum/palladium on active carbon, copper chromite, barium chromite, nickel/chromium oxide on alumina, cobalt sulfide, nickel sulfide, copper/molybdenum(VI)

oxide/silica/alumina catalysts, palladium on active carbon catalysts partially poisoned with selenium or lead, and the catalysts according to DE-A 3 932 332, US-A 3 449 445, EP-A 44444, EP-A 147 219, DE-A 3 904 083, DE-A 2 321 101, EP-A 415 202, DE-A 2 366 264 and EP-A 100 406.

Hydrogenation catalysts which contain Brönsted and/or Lewis acid centers may also advantageously be used in the novel process. For example, the catalytically active metals themselves may act as Brönsted or Lewis acid centers if they are not reduced completely to the relevant metals in the activation of the catalyst with hydrogen or hydrogen-containing gases. This applies, for example, to the chromite-containing catalysts, such as copper chromite. Furthermore, such Lewis or Brönsted acids or basic centers can be introduced into the catalyst via the carrier used. Examples of carriers containing Lewis or Brönsted acid centers are the aluminum oxides, titanium dioxides, zirconium dioxide, silica, the silicates, aluminas, zeolites, mixed magnesium/aluminum oxides and active carbon.

Supported catalysts which contain the elements of subgroups IA, VI, VII and/or VIII of the Periodic Table of Elements, in particular the elements of subgroups VII and VIII of the Periodic Table of Elements, deposited on a carrier acting as a Brönsted or Lewis acid are therefore preferably used as hydrogenation catalysts in the novel process. Particularly advantageous catalysts are, for example, ruthenium on active carbon, ruthenium on alumina, ruthenium on silica, ruthenium on magnesium oxide, ruthenium on zirconium dioxide, ruthenium on titanium dioxide, palladium on alumina, palladium on silica, palladium on zirconium dioxide, palladium on barium sulfate and palladium on active carbon catalysts partially poisoned with selenium or lead.

Lewis or Brönsted acid components, such as zeolites, aluminum oxides or silicas, phosphoric acid or sulfuric acid, may be added to catalysts which themselves have no such Brönsted or Lewis acid centers. They are added in general in amounts of from 0.01 to 5, preferably from 0.05 to 0.5, particularly preferably from 0.1 to 0.4, % by weight, based on the weight of the catalyst used.

Also suitable for the conversion of the allyl ether I into the acetal III are heterogeneous catalysts which contain the organometallic complex compounds of transition metals from group VIA and VIIIA of the Periodic Table of Elements in heterogeneous form, for example those in which the relevant transition metal is

fixed to a polymeric matrix, said complex compounds being capable of being used for the homogeneous catalysis of this process stage.

Such polymeric matrices may be resins, such as styrene/divinylbenzene resins or phenol/formaldehyde resins, to which the relevant ligands serving for complexing of the transition metal element are preferably covalently bonded, which ligands in turn form complexes with the relevant transition metals and thus virtually immobilize them.

Such heterogeneous, polymer-bonded complexes of group VIA or group VIIIA elements, in particular palladium and nickel complexes, are obtainable, for example, by the process of Zhuangyu et al. (Reactive Polymers 9 (1988), 249 or according to Wang et al. (J. Org. Chem. 59 (1994), 5358). Immobilized phosphine complexes of group VIA and VIIIA elements are obtainable, for example, by the processes of Hartley, Adv. Organomet. Chem. 15 (1977) 189, F.R. Hartley, Supported Metal Complexes, Riedel, Dordrecht 1985, K. Smith, Solid Supports and Catalysis in Organic Synthesis, Ellis Horwood, Prentice Hall, N.Y. 1992, C.H. Pittman, Polymer supported Reactions in Organic Synthesis, page 249, Wiley, Chichester 1980, and C.H. Pittmann J. Am. Chem. Soc. 98 (1976), 5407, and Ann. N.Y. Acad. Sci. 245 (1977), 15. The advantage of using such heterogeneous catalysts is in particular the easier and gentler separability of the catalyst from the reaction products. Said catalyst can be arranged in a fixed bed through which the reaction mixture flows or may be suspended in the reaction mixture and mechanically separated off after the end of the reaction.

The heterogeneous catalyst can be used either in suspension in the liquid reaction medium or, preferably, arranged in a fixed bed or plurality of fixed beds. When a heterogeneous catalyst suspended in the liquid reaction medium is used, the process can be carried out, for example, in stirred kettles or loop reactors. When a heterogeneous catalyst arranged in a fixed bed is used, the reaction mixture is passed over the fixed catalyst bed in general by the liquid-phase or trickle-bed procedure.

In general, the catalyst is loaded with the liquid reaction mixture at a space velocity of from 0.001 to 2, preferably from 0.01 to 1.5, particularly preferably from 0.05 to 1, kg of reaction mixture per l of catalyst per h. When the heterogeneous catalyst is used, the reaction can be carried out in the presence or absence of a solvent. The solvents used may be the same as

those which can also be used in carrying out the process under homogeneous catalysis.

The addition of the alcohol R^3OH II for producing the acetal III from the allyl ether I can be varied within wide ranges. The required equimolar amount can, if desired, also be exceeded. In general, the alcohol R^3OH II is fed to the reactor in a molar ratio II/I of from 1:1 to 100:1, preferably from 1:1 to 10:1, in particular from 1:1 to 5:1, based on the allyl ether I used in this reaction. A larger molar excess of the alcohol, based on the adduct, generally has no adverse effect on the result of the reaction, but the alcohol R^3OH II is advantageously used in the abovementioned ratios. The isomerization and acetalation of the allyl ether to give the acetal III over the heterogeneous catalyst in the liquid phase is carried out in general at from 20 to 300°C, preferably from 50 to 280°C, particularly preferably from 80 to 250°C, and at in general from 1 to 100, preferably from 1 to 50, in particular from 2 to 10, bar.

The liquid reaction discharge from this process stage is generally worked up by distillation in a manner similar to that described above for carrying out this process stage with homogeneous catalysts. When heterogeneous catalysts are used, the recycling of the catalyst, as may be expedient and advantageous in certain circumstances when using homogeneous catalysts, is of course omitted.

Acetals can be prepared in good yields and selectivities starting from allyl ethers by means of the novel process. In particular, the catalysts to be used in the novel process are distinguished by good separability from the reaction product and by good stability, with the result that the disadvantages of the prior art can be overcome.

Examples

Example 1

A glass autoclave was filled with 0.022 g of the catalyst $HRuCl(CO)(PPh_3)_3$, 0.031 g of triphenylphosphine, 0.005 g of decanoic acid, 3.18 g (24.8 mmol) of 1-butoxybut-2-ene and 1.83 g (24.8 mmol) of n-butanol. After a reaction time of 16 hours at 160°C under autogenous pressure, the reaction mixture was analyzed by means of calibrated gas chromatography. At a conversion of

85%, 1,1-dibutoxybutane was formed with a selectivity of 85.1% and 1-butoxybut-1-ene with a selectivity of 10.1%.

Example 2

A glass autoclave was filled with 0.10 g of the heterogeneous catalyst palladium on active carbon (10% by weight of Pd), 3.0 g (24 mmol) of 1-butoxybut-2-ene and 1.73 g (24 mmol) of n-butanol. After 16 hours at 150°C under a hydrogen atmosphere (1 bar), the reaction mixture was analyzed by means of calibrated gas chromatography. At a conversion of 21%, 1,1-dibutoxybutane was formed with a selectivity of 42%, dibutyl ether with a selectivity of 25% and 1-butoxybut-1-ene with a selectivity of 22%.

We claim:-

1. A process for the preparation of acetals by reacting allyl ethers with alcohols, wherein an allyl ether is reacted with an alcohol in the liquid phase in the presence of a homogeneous catalyst comprising an organometallic compound of an element of the platinum group metals or in the presence of a heterogeneous catalyst which contains one or more elements of the groups IA, VIA, VIIA and/or VIIIA of the Periodic Table of Elements, under essentially anhydrous conditions.

2. A process as claimed in claim 1, wherein the homogeneous catalyst used is a complex of a platinum metal with a monodentate or polydentate phosphine or phosphite ligand.

3. A process as claimed in claims 1 and 2, wherein the homogeneous catalyst is produced in situ in the reaction medium.

4. A process as claimed in claim 1, wherein the heterogeneous catalyst used is a supported catalyst.

5. A process as claimed in claim 1 and 4, wherein the heterogeneous catalyst used is a supported catalyst which contains aluminum oxide, titanium dioxide, zirconium dioxide, a silicate, an alumina, a zeolite and/or an active carbon as the carrier.

6. A process as claimed in claims 1 and 4 to 5, wherein a heterogeneous catalyst which contains palladium is used.

7. A process as claimed in claims 1 and 4 to 6, wherein a heterogeneous catalyst which additionally contains an element of group VA of the Periodic Table of Elements is used.

8. A process as claimed in claims 1 and 5 to 7, wherein a heterogeneous catalyst which additionally contains an element of group VA of the Periodic Table of Elements is used.

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