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(54) **INTRAMOLECULAR PRINS REACTION AND CATALYSTS SUITABLE THEREFOR (CITRONELLAL TO ISOPULEGOL)**

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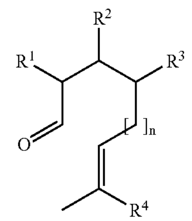
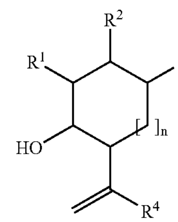
(57) **ABSTRACT**

Processes for the preparation of a compound of the formula (B) having the following steps: provision of a compound of the formula (A), intramolecular reaction of the compound of the formula (A) in the presence of an aluminium siloxide of the formula (I) wherein in formula (I) the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote hydrogen or an organic radical, are described.

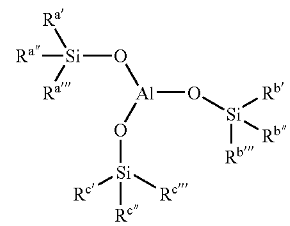
(A)



(B)

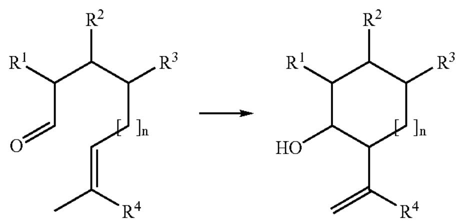


(I)



# INTRAMOLECULAR PRINS REACTION AND CATALYSTS SUITABLE THEREFOR (CITRONELLAL TO ISOPULEGOL)

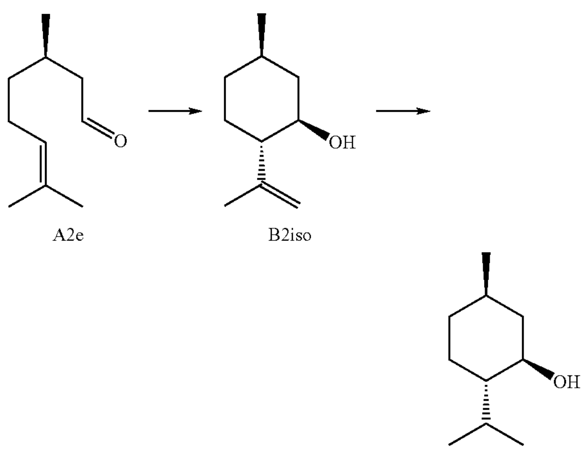
**[0001]** The present invention relates to a process for the preparation of a compound of the formula B from a compound of the formula A by an intramolecular Prins reaction (also known as intramolecular carbonyl-ene or oxygen-ene reaction), catalysts for this reaction (in particular based on aluminium- and silicon-containing compounds). Processes for the preparation of the catalysts and the use of certain substances as catalysts, in particular in the processes mentioned, are furthermore described.



A B

**[0002]** A known examples of an intramolecular Prins reaction is the cyclization of citronellal (3,7-dimethyl-6-octenal, A2) to isopulegol and its stereoisomers (8-p-menthen-3-ol; B2, i.e. isopulegol, neoisopulegol, isoisopulegol and neoisoisopulegol).

**[0003]** Isopulegol is of great interest for use as an odoriferous and aroma substance and can furthermore be converted into menthol by hydrogenation, as is shown in the following equation starting from d-citronellal (A2e) to give l-menthol (Ze) via l-isopulegol (B2 iso).



A2e B2iso

Ze

**[0004]** Depending on the stereochemical composition of the starting material A and the selectivity of the cyclization reaction, the product B formed can comprise a large number of stereoisomers (diastereostereomers and, where appropriate, enantiomers). A reaction procedure which is as selective as possible to give a particular diastereomer is usually aimed for.

**[0005]** The cyclization of d-citronellal to l-isopulegol in the presence of various Lewis acids is described in Synthesis 1978, 147, the best results (70% yield) having been achieved with equimolar amounts of zinc bromide in benzene. In this reaction, intermolecular addition products, inter alia, are observed as undesirable by-products, for example from the aldol condensation or the intermolecular Prins reaction. The 1-isopulegol sought is formed with a selectivity of 94%, and a content of 6% is thus due to the further isopulegol isomers, d-neoisopulegol predominating among these isomers and the other isomers being formed only in traces.

**[0006]** In addition, the cyclization of citronellal to give isopulegol has been attempted in the presence of numerous other (Lewis acid) catalysts, and in this respect reference may be made to the summary in EP 1 225 163 A2.

**[0007]** The possibility of separating off and re-using a Lewis acid from an aqueous medium after cyclization of citronellal to isopulegol has taken place is described in EP 1 053 974 A1. Using 34-40 mol % of (recyclized) zinc bromide as the catalyst, GC yields of isopulegol in the range of from about 82 to 89 GC % were obtained, the citronellal employed already containing more than 4% of isopulegol. In addition to the disadvantages of zinc bromide per se (heavy metal, poor handling), a difficult and energy-consuming separating off of the catalyst from the aqueous phase must be carried out in this process.

**[0008]** J. Am. Chem. Soc. 1980, 102, 7951-7953 describes the cyclization of citronellal to isopulegol in the presence of a molar equivalent of $Me_2AlCl$, isopulegol and neoisopulegol chiefly being obtained.

**[0009]** EP 1 225 163 A2 describes the conversion of citronellal into isopulegol using tris(2,6-diarylphenoxy)aluminium catalysts. Isopulegol is obtained in yields of up to more than 95% and with a selectivity of more than 99% starting from citronellal. Nevertheless, the catalysts employed are quite unstable and cannot be re-used or recycled when the reaction has ended. They are sensitive towards higher temperatures and aqueous media, and their preparation and handling present problems. A re-use of the tris(2,6-diarylphenoxy)aluminium catalysts disclosed is accordingly not described.

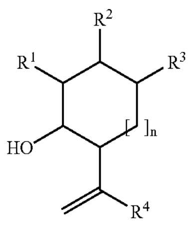
**[0010]** From the technical aspect, the catalyst systems to date are disadvantageous because of their sensitivity to exposure to heat and/or aqueous media. Re-usability or recycling is either not possible at all, or possible only with a high outlay.

**[0011]** There therefore continues to be a need for processes and catalyst systems which render possible the preparation of cyclization products in a good yield by means of an intramolecular Prins reaction, and allows simple isolation of the cyclization products, preferably by means of the separation processes which are usual in industry, such as, for example, distillation. The catalyst system should preferably be re-usable or recyclable and have substantially constant properties in respect of activity and selectivity (in formation of the cyclization products) over several reaction cycles.

**[0012]** The present invention is based on the object of providing such an improved process or catalyst system. In particular, the process and catalyst system should render possible a chemo- and diastereoselective cyclization of citronellal to isopulegol with the preferential formation of l-isopulegol.

**[0013]** The object described in respect of the "process" aspect is achieved according to a first alternative by a process for the preparation of a compound of the formula B

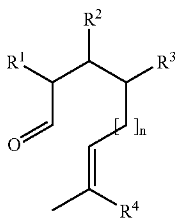
B



having the following steps:

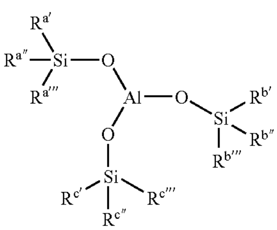
**[0014]** provision of a compound of the formula A

A



**[0015]** intramolecular reaction of the compound of the formula A in the presence of an aluminium siloxide of the formula (I)

(I)



wherein in the formulae A and B the meaning of $R^1$, $R^2$, $R^3$ and n is identical and;

$R^1$, $R^2$, $R^3$ in each case independently of one another denote hydrogen or methyl, $R^4$ denotes hydrogen or an alkyl radical having 1 to 6 C atoms, n denotes 0, 1 or 2

and wherein in formula (I):

$R^{a'}$, $R^{a''}$, $R^{a''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote hydrogen or an organic radical (having preferably not more than 100 C atoms), preferably an optionally substituted radical chosen from the group consisting of alkyl, heteroalkyl, cycloalkyl, cycloalkylalkyl, alkenyl, cycloalkenyl, cycloalkenylalkyl, alkynyl, cycloalkylalkynyl, alkoxy, cycloalkoxy, cycloalkylalkoxy, aryl, heteroaryl, arylalkyl, cycloalkylaryl, cycloalkenylaryl, cycloalkylheteroaryl, heterocycloalkylaryl, heterocycloalkenylaryl, heterocycloalkenylheteroaryl and heteroarylalkyl, with the proviso that at least one of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$ and one of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and one of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ is not hydrogen;

wherein independently of one another also two or three of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, two or three of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and two or three of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ can be covalently bonded to one another,

**[0016]** If the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$ and $R^{c'''}$ are substituted, the following substituents are preferred:

hydroxyl,

$C_1$-$C_8$-alkyl, preferably methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl,

$C_3$-$C_{18}$-cycloalkyl, preferably cyclopropyl, cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, cyclopentadecyl, cyclohexadecyl,

$C_2$-$C_8$-alkynyl, preferably ethynyl, propynyl,

$C_1$-$C_8$-perfluoroalkyl, preferably trifluoromethyl, nonafluorobutyl,

$C_1$-$C_8$-alkoxy, preferably methoxy, ethoxy, iso-propoxy, n-butoxy, iso-butoxy, tert-butoxy,

$C_3$-$C_{12}$-cycloalkoxy, preferably $C_3$-cycloalkoxy, $C_5$-cycloalkoxy, $C_6$-cycloalkoxy, $C_8$-cycloalkoxy, $C_{12}$-cycloalkoxy, $C_{15}$-cycloalkoxy, $C_{16}$-cycloalkoxy,

$C_1$-$C_{20}$-alkoxyalkyl, in which 1 to 5 $CH_2$ groups are replaced by oxygen, preferably —[—O—$CH_2$—$CH_2$—]$_v$-Q or —[—O—$CH_2$—CHMe-]$_v$-Q, wherein Q is OH or $CH_3$ and wherein v can denote 1 to 4,

$C_1$-$C_4$-acyl, preferably acetyl,

$C_1$-$C_4$-carboxyl, preferably $CO_2Me$, $CO_2Et$, $CO_2$ iso-Pr, $CO_2$tert-Bu,

$C_1$-$C_4$-acyloxy, preferably acetyloxy,

halide, preferably F or Cl,

$Si_1$-$Si_{10}$-silyl, and

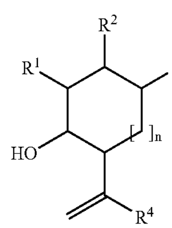
$Si_1$-$Si_{30}$-siloxy or polysiloxy.

**[0017]** If one or more of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$ and $R^{c'''}$ contains nitrogen, this nitrogen-containing radical is preferably stable to oxidation. In particular, under the oxidation conditions which prevail during the preparation of the silanols of the formulae (IIa), (IIb) and (IIc) described below, the nitrogen-containing radical should be inert, i.e. should not react with the oxidizing agent used there. Stability to oxidation can be achieved, for example, by the introduction of N-protective groups, such as N-acylation, or by quaternization of the nitrogen atom.

**[0018]** The aluminium siloxides tris-triphenylsiloxyaluminium $Al(OSiPh_3)_3$ and tris-triethylsiloxyaluminium $Al(OSiEt_3)_3$ which are suitable for use in the process according to the invention have been described in Can. J. Chem. 1992, 70, 771-778, $Al(OSiPh_3)_3$ being characterized in the form of its THF or THF-$H_2O$ adduct; a use of these aluminium siloxides as catalysts has not been described.

**[0019]** According to a further aspect of the present invention, the object described is achieved by a process for the preparation of a compound of the formula B

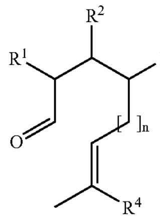
B



having the following steps:

**[0020]** provision of a compound of the formula A

A



**[0021]** mixing and/or reaction either of an aluminium compound of the formula (III)

$$H_pAl(R^5)_{3-p} \quad (III)$$

wherein

$R^5$ denotes an alkyl radical having 1 to 4 C atoms or an aryl radical and

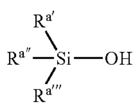
p is chosen from 0, 1 or 2,

or of an aluminium compound of the formula (IV)

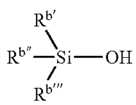
$$MAlH_4 \quad (IV)$$

wherein M is chosen from lithium, sodium or potassium, with silanols of the formulae (IIa), (IIb) and (IIc),

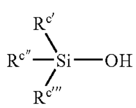
(IIa)



(IIb)



(IIc)



which can be identical or different,

wherein:

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote hydrogen or an organic radical, preferably an optionally substituted radical chosen from the group consisting of alkyl, heteroalkyl, cycloalkyl, cycloalkylalkyl, alkenyl, cycloalkenyl, cycloalkenylalkyl, alkynyl, cycloalkylalkynyl, alkoxy, cycloalkoxy, cycloalkylalkoxy, aryl, heteroaryl, arylalkyl, cycloalkylaryl, cycloalkenylaryl, cycloalkylheteroaryl, heterocycloalkylaryl, heterocycloalkenylaryl, heterocycloalkenylheteroaryl and heteroarylalkyl, with the proviso that at least one of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$ and one of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and one of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ is not hydrogen,

wherein independently of one another also two or three of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, two or three of the radicals $R^{b'}$, $R^{b''}$, $R^{b}$ and two or three of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ can be covalently bonded to one another,

**[0022]** Intramolecular reaction of the compound of the formula A in the presence of the mixture and/or the reaction product of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc).

**[0023]** Mixing and/or reaction of the aluminium compound of the formula (III) or (IV) with the silanols of the formulae (II), (IIb) and (IIc) conventionally results in the aluminium siloxides of the formula (I). However, working up and optionally characterization, for example, of the reaction products of the reaction is not necessary according to the invention.

**[0024]** Preferred processed according to the invention (according to the abovementioned aspects) are those wherein in the particular formulae A and B:

$R^1$ and $R^2$ in each case independently of one another denote hydrogen or methyl,

$R^3$ denotes hydrogen,

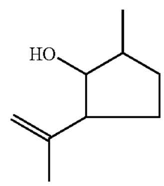
$R^4$ denotes methyl,

n denotes 0 or 1.

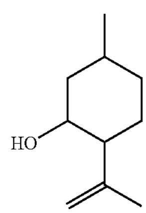
**[0025]** Particularly preferred processes according to the invention are those in which the compound of the formula A is chosen from the group consisting of 2,6-dimethyl-5-heptenal and citronellal (3,7-dimethyl-6-octenal; A2).

**[0026]** The preferred compounds B1 and B2 can be prepared from these compounds A of the formula A.

B1



B2



**[0027]** Preferably, the aluminium siloxide of the formula (I) or the reaction product of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc) is prepared in situ and/or is freshly prepared.

**[0028]** The preparation of the aluminium siloxides of the formula (I) can be carried out via the reaction of trialkylaluminium compounds with the corresponding silanols analogously to Can. J. Chem. 1992, 70, 771-778. For the preferred preparation process, see below.

**[0029]** In the context of the present invention, it has been found, surprisingly, that the catalysts to be employed according to the invention, i.e. the aluminium siloxides of the formula (I) having the abovementioned meaning of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$ and $R^{c'''}$ or the said reaction products and mixtures of aluminium compound and silanols render possible in an extremely selective manner the conversion of compounds of the formula A into the compounds of the formula B, in particular of A2 into B2.

**[0030]** The catalysts are distinguished by an easy and flexible accessibility and a high stability, in particular a high heat stability and a stability towards aqueous media.

**[0031]** The intramolecular Prins reaction using the catalysts to be employed according to the invention, in particular of the formula (I), for the preparation of isopulegol (B2) from citronella (A2) is distinguished in that isopulegol and neoisopulegol are chiefly obtained with a very high selectivity over a wide temperature range, and the diastereomers isoisopulegol and neoisoisopulegol are formed only in traces. For the selectivities to be achieved and the temperatures suitable for carrying out the reaction, see below.

**[0032]** In our own studies starting from citronellal (A2), it was found, compared with the tris(2,6-diarylphenoxy)aluminium catalysts according to EP 1 225 163 A2 which are described above, that the intramolecular Prins reaction proceeds significantly faster in the presence of the catalysts to be employed according to the invention, in particular of the formula (I). The catalysts to be employed according to the invention, in particular of the formula (I), are significantly more stable towards exposure to heat and towards aqueous media than those described in EP 1 225 163 A2. Furthermore, when the tris(2,6-diarylphenoxy)aluminium catalysts according to EP 1 225 163 A2 were employed, in addition to the formation of the desired cyclization products (in particular B2), the intermolecular ester formation according to the Tischtschenko-Claisen reaction is also observed to a small extent.

**[0033]** In preferred processes according to the invention, the intramolecular reaction of the compound of the formula A is carried out in a diluent, the boiling point of which is higher than that of the compounds of the formulae A and B

or

after the intramolecular reaction of the compound of the formula A has taken place, a diluent, the boiling point of which is higher than that of the compounds of the formulae A and B, is added, Such a process conventionally comprises the following further step:

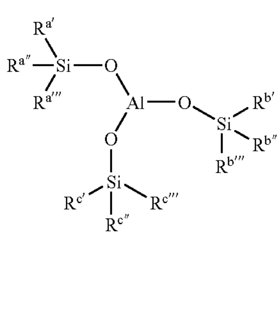
**[0034]** separating off, by distillation, of the compound of the formula B from the diluent and the aluminium siloxide of the formula (I) or the reaction product of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc). Details of these preferred process embodiments are given below.

**[0035]** The catalyst (aluminium siloxide of the formula (I) or mixtures and/or reaction product of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc)) employed in the process according to the invention is re-usable and recyclable. The aluminium siloxide of the formula (I) or the mixture and/or the reaction product of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc)) is accordingly preferably employed again in the intramolecular reaction of the compound of the formula A. In this context also, details are given below.

**[0036]** The present invention also relates to the use

**[0037]** either of an aluminium siloxide of the formula (I)

(I)



**[0038]** or of a mixture and/or a reaction product of a reaction

either of an aluminium compound of the formula (III)

$$H_pAl(R^5)_{3-p} \qquad \text{(III)}$$

wherein

$R^5$ denotes an alkyl radical having 1 to 4 C atoms or an aryl radical and

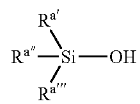
p is chosen from 0, 1 or 2,

or of an aluminium compound of the formula (IV)

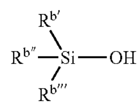
$$MAlH_4 \qquad \text{(IV)}$$

wherein M is chosen from lithium, sodium or potassium, with silanols of the formulae (IIa), (IIb) and (IIc),

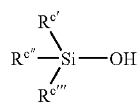
(IIa)



(IIb)



(IIc)



which can be identical or different,

wherein in the formula (I) and the formulae (IIa), (IIb) and (IIc);

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote hydrogen or an organic radical, preferably an optionally substituted radical chosen from the group consisting of alkyl, heteroalkyl, cycloalkyl, cycloalkylalkyl, alkenyl, cycloalkenyl, cycloalkenylalkyl, alkynyl, cycloalkylalkynyl, alkoxy, cycloalkoxy, cycloalkylalkoxy, aryl, heteroaryl, arylalkyl, cycloalkylaryl, cycloalkenylaryl, cycloalkylheteroaryl, heterocycloalkylaryl, heterocycloalkenylaryl, heterocycloalkenylheteroaryl and heteroarylalkyl, with the proviso that at least one of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$ and one of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and one of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ is not hydrogen,

wherein independently of one another also two or three of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, two or three of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and two or three of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ can be covalently bonded to one another,

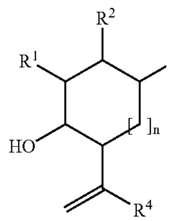
as a catalyst.

**[0039]** If the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$ and $R^{c'''}$ are substituted, the abovementioned substituents are preferred.

**[0040]** As already emerges from the statements regarding the process according to the invention, the use for catalysis of intramolecular Prins reactions is preferred.

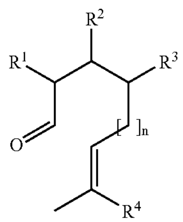
**[0041]** As likewise already emerges from the statements regarding the processes according to the invention, a particularly preferred use is that for the preparation of a compound of the formula B

B



from of a compound of the formula A

A



wherein in the formulae A and B $R^1$, $R^2$, $R^3$ and n in each case have the same meaning and:

$R^1$, $R^2$, $R^3$ in each case independently of one another denote hydrogen or methyl, $R^4$ denotes hydrogen or an alkyl radical having 1 to 6 C atoms, n denotes 0, 1 or 2.

**[0042]** In preferred processes according to the invention and preferred uses according to the invention, for the aluminium siloxide of the formula (I) and the silanols of the formulae (IIa), (IIb) and (IIc), preferably:

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote an optionally substituted radical chosen from the groups consisting of $C_1$-$C_{20}$-alkyl, $C_1$-$C_{20}$-heteroalkyl, $C_3$-$C_{20}$-cycloalkyl, $C_4$-$C_{20}$-cycloalkylalkyl, $C_2$-$C_{20}$-alkenyl, $C_3$-$C_{20}$-cycloalkenyl, $C_4$-$C_{20}$-cycloalkenylalkyl, $C_2$-$C_{20}$-alkynyl, $C_5$-$C_{20}$-cycloalkylalkynyl, $C_1$-$C_{20}$-alkoxy, $C_3$-$C_{20}$-cycloalkoxy, $C_5$-$C_{10}$-cycloalkylalkoxy, $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{25}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_8$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl,

wherein independently of one another also two or three of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, two or three of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and two or three of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ can be covalently bonded to one another,

**[0043]** In this context, $R^{a'}$ to $R^{c''}$ preferably independently of one another denote an optionally substituted radical chosen from the group consisting of $C_1$-$C_{10}$-alkyl, $C_3$-$C_{10}$-cycloalkyl, $C_4$-$C_{12}$-cycloalkylalkyl, $C_2$-$C_{10}$-alkenyl, $C_3$-$C_{12}$-cycloalkenyl, $C_4$-$C_{12}$-cycloalkenylalkyl, $C_2$-$C_{10}$-alkynyl, $C_5$-$C_{12}$-cycloalkylalkynyl, $C_3$-$C_{20}$-aryl, $C_2$-$C_{20}$-heteroaryl, $C_4$-$C_{20}$-arylalkyl, $C_8$-$C_{20}$-cycloalkylaryl, $C_8$-$C_{20}$-cycloalkenylaryl, $C_5$-$C_{20}$-cycloalkylheteroaryl, $C_8$-$C_{20}$-heterocycloalkylaryl, $C_8$-$C_{20}$-heterocycloalkenylaryl, $C_8$-$C_{20}$-heterocycloalkenylheteroaryl or $C_4$-$C_{20}$-heteroarylalkyl.

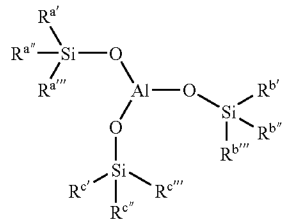
**[0044]** Particularly preferably:

$R^{a'}$ to $R^{c'''}$ independently of one another denote an optionally substituted radical chosen from the group consisting of $C_1$-$C_{10}$-alkyl, $C_3$-$C_{10}$-cycloalkyl, $C_4$-$C_{12}$-cycloalkylalkyl, $C_6$-$C_{20}$-aryl, $C_2$-$C_{20}$-heteroaryl, $C_7$-$C_{20}$-arylalkyl, $C_8$-$C_{20}$-cycloalkylaryl, $C_8$-$C_{20}$-cycloalkenylaryl, $C_6$-$C_{20}$-cycloalkylheteroaryl, $C_8$-$C_{20}$ heterocycloalkylaryl, $C_8$-$C_{20}$-heterocycloalkenylaryl, $C_8$-$C_{20}$-heterocycloalkenylheteroaryl or $C_4$-$C_{20}$-heteroarylalkyl.

**[0045]** A further aspect of the present invention relates to novel catalysts and Lewis acids which are suitable in particular for use in the processes described above. The best results were achieved in the processes described above using these novel catalysts and Lewis acids.

**[0046]** Preferred catalysts and Lewis acids are aluminium siloxides of the formula (I)

(I)



wherein:

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote an optionally substituted radical chosen from the group consisting of $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{25}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_8$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl,

excluding the compounds known from Can. J. Chem. 1992, 70, 771-778, in particular the compound $Al(OSiPh_3)_3$.

**[0047]** A catalyst which can likewise be employed, in particular in the processes described above, is a mixture either of an aluminium compound of the formula (III)

$$H_pAl(R^5)_{3-p} \quad \text{(III)}$$

wherein

$R^5$ denotes an alkyl radical having 1 to 4 C atoms or an aryl radical and

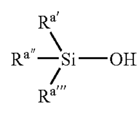
p is chosen from 0, 1 or 2,

or of an aluminium compound of the formula (IV)

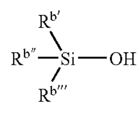
$$MAlH_4 \quad \text{(IV)}$$

wherein M is chosen from lithium, sodium or potassium, with silanols of the formulae (IIa), (IIb) and (IIc),

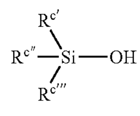
(IIa)



(IIb)



(IIc)



which can be identical or different,
wherein in the formula (I) and the formulae (IIa), (IIb) and (IIc):
$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote an optionally substituted radical chosen from the group consisting of $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{25}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_8$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl,
wherein the mixture comprises no $AlMe_3$ and/or $HOSiPh_3$.

**[0048]** The catalytic activity of such a mixture is presumably based on the formation of aluminium siloxide of the formula (I); however, this is not clarified conclusively.

**[0049]** A catalyst which can likewise be employed, in particular in the processes described above, is the (purified or non-purified) reaction product of a reaction either of an aluminium compound of the formula (III)

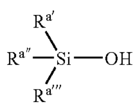
$$H_pAl(R^5)_{3-p} \tag{III}$$

wherein
$R^5$ denotes an alkyl radical having 1 to 4 C atoms or an aryl radical and
p is chosen from 0, 1 or 2,
or of an aluminium compound of the formula (IV)

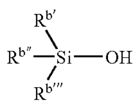
$$MAlH_4 \tag{IV}$$

wherein M is chosen from lithium, sodium or potassium, with silanols of the formulae (IIa), (IIb) and (IIc),

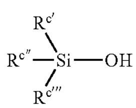
(IIa)



(IIb)



(IIc)



which can be identical or different,
wherein in the formula (I) and the formulae (IIa), (IIb) and (IIc):
$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote an optionally substituted radical chosen from the group consisting of $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{26}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_8$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl,
excluding the compound $Al(OSiPh_3)_3$.

**[0050]** Preferred catalysts according to the invention are the aluminium siloxides, mixtures and reaction products just defined, wherein in each case:
$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c'''}$, $R^{c'''}$ independently of one another denote an optionally substituted radical chosen from the group consisting of $C_6$-$C_{20}$-aryl, $C_3$-$C_{20}$-heteroaryl, $C_7$-$C_{20}$-arylalkyl, $C_8$-$C_{20}$-cycloalkylaryl, $C_8$-$C_{20}$-cycloalkenylaryl, $C_6$-$C_{20}$-cycloalkylheteroaryl, $C_8$-$C_{20}$-heterocycloalkylaryl, $C_8$-$C_{20}$-heterocycloalkenylaryl, $C_8$-$C_{20}$-heterocycloalkenylheteroaryl and $C_4$-$C_{20}$-heteroarylalkyl.

**[0051]** Aluminium siloxides, mixtures and reaction products which are particularly preferred for use as catalysts and Lewis acids in the processes according to the invention are those for which:
$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another denote an optionally substituted radical chosen from the group consisting of $C_6$-$C_{20}$-aryl, $C_3$-$C_{20}$-heteroaryl, $C_8$-$C_{20}$-cycloalkylaryl, $C_8$-$C_{20}$-cycloalkenylaryl, $C_7$-$C_{20}$-cycloalkylheteroaryl, $C_8$-$C_{20}$-heterocycloalkylaryl, $C_8$-$C_{20}$-heterocycloalkenylaryl and $C_8$-$C_{20}$-heterocycloalkenylheteroaryl.

**[0052]** Particularly preferred radicals $R^{a'}$ to $R^{c'''}$ from the group consisting of $C_6$-$C_{20}$-aryl are: phenyl, 4-methoxyphenyl, 2,4-dimethoxyphenyl, 4-methylphenyl, 2,4-dimethylphenyl, 3,5-dimethylphenyl, 2-tert-butylphenyl, 4-tert-butylphenyl, 2,6-di-tert-butylphenyl, 4-$CF_3$-phenyl, 2,4-di-$CF_3$-phenyl, 1-naphthyl, 2-naphthyl, 9-anthracenyl, 9-phenanthrenyl.

**[0053]** Particularly preferred radicals $R^{a'}$ to $R^{c'''}$ from the group consisting of $C_3$-$C_{20}$-heteroaryl are: 2-furfuryl, 3-furfuryl, imidazolyl.

**[0054]** Particularly preferred radicals $R^{a'}$ to $R^{c'''}$ from the group consisting of $C_8$-$C_{20}$-cycloalkylaryl are: indanyl, fluorenyl.

**[0055]** Particularly preferred radicals $R^{a'}$ to $R^{c'''}$ from the group consisting of $C_8$-$C_{20}$-cycloalkenylaryl are: indenyl.

**[0056]** Particularly preferred radicals $R^{a'}$ to $R^{c'''}$ from the group consisting of $C_8$-$C_{20}$-heterocycloalkenylaryl are: N—$C_1$-$C_{18}$-alkyl- or N—$C_1$-$C_8$-acyl-indolyl.

**[0057]** Particularly preferred radicals $R^{a'}$ to $R^{c'''}$ from the group consisting of $C_6$-$C_{20}$-heterocycloalkylaryl are: N—$C_1$-$C_{16}$-alkyl- or N—$C_1$-$C_8$-acyl-indolinyl.

**[0058]** Examples of particularly preferred catalysts of the formula (I) are:

| Compound of the formula (I) | $R^{a'}$-$R^{a'''}$ | $R^{b'}$,$R^{b''}$ | $R^{b'''}$ | $R^{c'}$-$R^{c'''}$ |
|---|---|---|---|---|
| 1 | Ph | Ph | Ph | Ph |
| 2 | 4-Me-Ph | Ph | 2,6-di-tert-butyl-Ph | Ph |
| 3 | 4-$CF_3$-Ph | 2-naphthyl | 2-naphthyl | 4-$CF_3$-Ph |
| 4 | 1-naphthyl | 1-naphthyl | 1-naphthyl | 1-naphthyl |
| 5 | 9-anthracenyl | Ph | Ph | Ph |
| 6 | 4-MeO-Ph | Ph | Ph | 4-MeO-Ph |
| 7 | 2-furfuryl | Ph | Ph | Ph |
| 8 | indenyl | Ph | Ph | indenyl |
| 9 | fluorenyl | fluorenyl | fluorenyl | fluorenyl |
| 10 | 2-naphthyl | 2-naphthyl | 2-naphthyl | 2-naphthyl |

Abbreviations used: tert = tertiary, Ph = phenyl, Me = methyl

**[0059]** Preferred processes, uses, aluminium siloxides, mixtures and reaction products according to the invention are those wherein, for the aluminium siloxide of the formula (I) and the silanols of the formulae (IIa), (IIb) and (IIc):

**[0060]** The radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$ are identical, the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ are identical and the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ are identical,
and preferably all the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ are identical. The preparation of the aluminium siloxide catalysts (Lewis acids) of the formula (I) is easiest namely if the particular radicals bonded to the same Si atom

in the formula (I) are identical, i.e. $R^{a'}=R^{a''}=R^{a'''}$ *und* $R^{b'}=R^{b''}=R^{b'''}$ und $R^{c'}=R^{c''}=R^{c'''}$. Catalysts of the formula (I) in which all the radicals $R^{a'}$ to $R^{c'''}$ have the same meaning are particularly easy to prepare, such as, for example, in the case of tris-triphenylsiloxyaluminium $Al(OSiPh_3)_3$.

**[0061]** The catalysts (aluminium siloxide, mixtures and reaction products) to be employed according to the invention are particularly stable, which is advantageous for the use of the catalysts under industrial conditions, in particular since in contrast to the known systems the catalysts have a higher heat stability. The processes according to the invention can be carried out in a wide temperature range without loss in the selectivity, and lead reliably to the intramolecular reaction products sought.

**[0062]** The catalysts to be employed according to the invention (and in particular the novel aluminium siloxides of the formula (I) according to the invention) are advantageously distinguished in that at comparatively high concentrations of compounds of the formula A, compared with the known Al-based catalysts, there is only a very slight tendency towards the formation of Tischtschenko-Claisen products. The diastereoselectivity is also particularly and surprisingly high when the catalysts to be used according to the invention are employed.

**[0063]** The preparation of catalysts for use in processes according to the invention, in particular the preparation of aluminium siloxides of the formula (I), can preferably be carried out starting from aluminium compounds of the formula (III)

$$H_pAl(R^5)_{3-p} \qquad \text{(III)}$$

wherein

$R^5$ denotes an alkyl radical having 1 to 4 C atoms or an aryl radical and

p is chosen from 0, 1 or 2.

**[0064]** Alternatively, the starting compounds are preferably aluminium compounds of the formula (IV)

$$MAlH_4 \qquad \text{(IV)}$$

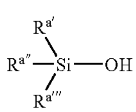
wherein M is chosen from lithium, sodium or potassium and is preferably lithium.

**[0065]** Preferably, the aluminium compound (III) is chosen from the group consisting of trimethylaluminium, triethylaluminium, tripropylaluminium, tributylaluminium, triphenylaluminium, dimethylaluminium hydride, diethylaluminium hydride, dipropylaluminium hydride, dibutylatuminium hydride, methylaluminium dihydride, ethylaluminium dihydride, propylaluminium dihydride and butylaluminium dihydride, and trimethylaluminium and triethylaluminium are preferred.

**[0066]** The aluminium compound (IV) is preferably lithium aluminium hydride.

**[0067]** The preparation of the catalysts of the formula (I) is preferably carried out by addition of the aluminium compound of the formula (Ill) or (IV) to a solution or dispersion of silanols of the formulae (IIa), (IIb) and (IIc)

(IIa)



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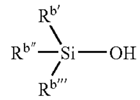
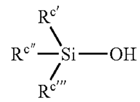
(IIb)



(IIc)



wherein

the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$ and $R^{c'''}$ in each case have the abovementioned (preferred) meaning. The silanols (IIa), (IIb) and (IIc) can be identical or different; if they are identical, the three siloxy groups in the aluminium siloxide of the formula (I) are also identical.

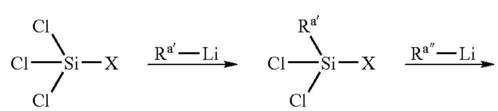
**[0068]** The molar ratio of the total amount of silanol(s) of the formulae (IIa), (IIb) and (IIc) to the amount of aluminium compound of the formula (III) or (IV) in the mixtures according to the invention and/or in the reaction of the aluminium compound of the formula (III) or (IV) with the silanols is at least 3, and the molar ratio is preferably in the range of from 3 to 6, preferably in the range of from 3 to 5.

**[0069]** The preparation of the aluminium siloxide of the formula (I) or the reaction product of the reaction of the aluminium compound with the silanols is conventionally carried out in diluents (preferably solvents) which are inert for the reactants, such as e.g. aromatic hydrocarbons, such as benzene, toluene or xylene (in this case preferably toluene), aliphatic hydrocarbons (such as heptane) or ethers (such as diethyl ether, diisopropyl ether or tetrahydrofuran). The aluminium siloxide of the formula (I) or the reaction products of the reaction of the aluminium compound with the silanols can also be prepared in high-boiling diluents, such as diphenyl ether or ditolyl ether. It is furthermore possible to prepare the aluminium siloxide of the formula (I) or the said reaction product in the same diluent in which the intramolecular Prins reaction is carried out (see below, in particular the examples).

**[0070]** The content of silanol or silanols of the formulae (IIa), (IIb) and (IIc) in the reaction mixture in the (in situ) generation of the catalyst is not decisive for the reaction with the aluminium compound of the formula (III) or (IV). The total content of silanols of the formulae (IIa), (IIb) and (IIc) is preferably between 30 and 1 wt. %, preferably between 20 and 5 wt. %, based on the total weight of the reaction mixture. The best results in the (in situ) preparation of catalysts of the formula (I) were obtained with total contents of compounds of the formulae (IIa), (IIb) and (IIc) of between 7.5 and 12.5 wt. %, based on the total weight of the reaction mixture.

**[0071]** The time required for the formation of an aluminium siloxide of the formula (I) is usually in the range of from 5 to 60 minutes.

**[0072]** Silanols of the formulae (IIa), (IIb) and (IIc) can be prepared, for example, by the following reaction route, as shown by way of example for (IIa);



X = H, Cl

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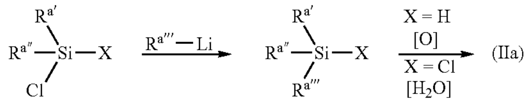


**[0073]** The statements above and below regarding the preparation of the silanols of the formula (IIa) apply accordingly to the preparation of the silanols of the formula (IIb) and (IIc). References to formula (IIa) also otherwise correspond to no references to the formula (IIb) and (IIc).

**[0074]** Depending on the desired substitution pattern, for the preparation of (IIa) (and the same also applies, as mentioned, for (IIb) and (IIc)), for example starting from the chlorosilanes $HSiCl_3$ (see the above reaction route, X═H), $H_2SiCl_2$ or $H_3SiCl$, the chlorine atoms of the chlorosilane can be exchanged successively or, if the radicals $R^a$ to $R^{a''}$ are identical, also in one reaction step for the organic radical, preferably in the form of the corresponding lithium organyl (see the above reaction route and the examples below). A conversion of the silane formed in this way into the silanol of the formula (IIa) is then carried out by means of oxidation, for example with $KMnO_4$, in accordance with the process described in J. Organomet. Chem. 1995, 521, 229. The oxidation of the silanes can furthermore be carried out by other oxidation reagents, which likewise lead to the desired silanol of the formula (IIa) in high yields, such as e.g. ozone (Russ. Chem. Rev. 46 (10) 1977), homogeneous or heterogeneous ruthenium catalysts and water (J. Chem. Research 1997, 400) or also by free-radical reaction with N-hydroxyphthalimide (Synlett 2002, 7, 1173).

**[0075]** Starting from $SiCl_4$ (see the above reaction route, X═Cl), chlorosilanes of the type $(R^{a'})(R^{a''})(R^{a'''})SiCl$ can be prepared by sequential substitution, and can be converted into silanols of the formula (IIa) by subsequent hydrolysis of the Si—Cl bond. For example, commercially obtainable tert-butyl-chloro-diphenylsilane can be converted by means of hydrolysis into tert-butyldiphenylsilanol, for which in formula (IIa): $R^{a'}$=$R^{a'''}$=phenyl, $R^{a''}$=tert-butyl.

**[0076]** Preferably, lithium organyls or magnesium organyls, preferably lithium organyls, which contain the radicals $R^{a'}$ to $R^{a''}$, $R^{b'}$ to $R^{b'''}$ and $R^{c'}$ to $R^{c'''}$ are reacted with chlorosilanes in order to link the said radicals with the central Si atom. For the preparation of the lithium organyls, depending on the structure and CH acidity of the organyl, for example the corresponding bromine or iodine organyls can be used as starting substances (metal-halogen exchange) or, if the CH acidity is adequate, a direct lithiumation can be carried out. In both cases, the organyl is reacted with metallic lithium or a lithium-alkyl (such as, for example, methyllithium or butyllithium).

**[0077]** Some silanols of the formula (IIa) are commercially obtainable, such as, for example, triphenylsilanol, triethylsilanol or tert-butyldimethylsilanol. Furthermore, certain silanols of the formula (IIa) can be prepared from commercially obtainable compounds, such as chloromethyldiphenylsilane $MeSi(Ph)_2Cl$, by means of hydrolysis, or from dichlorodiphenylsilane $Ph_2SiCl_2$, for example by reaction with $R^{a'''}$-Li analogously to the above equation to give $Ph_2Si(R^{a'})Cl$, from which an unsymmetric silanol of the formula (IIa) is obtained after hydrolysis, compare Example 2 below.

**[0078]** The aluminium siloxide of the formula (I) or the said reaction product of the reaction of the aluminium compound (II) or (IV) with the silanols (IIa), (IIb) and (IIc) can be employed in substance or in a mixture with a diluent; the latter variant is advantageous in particular if the catalyst is to be freshly prepared and/or prepared (in situ) (in this context, see above).

**[0079]** The intramolecular Prins reaction can be carried out in the presence of one or more diluents or also without a diluent. In the diluent-free reaction procedure, a stirrability or homogenization of the reaction mixture is ensured by educt A and/or reaction product B.

**[0080]** Suitable diluents for carrying out the intramolecular Prins reaction are, for example, aromatic hydrocarbons, such as benzene, toluene, xylene, diphenyl, diphenylethane (dibenzyl), dodecylbenzene or dibenzylbenzenes, saturated hydrocarbons, such as hexane, heptane, octane, cyclohexane or methylcyclohexane, ethers, such as diethyl ether, diisopropyl ether, tetrahydrofuran, dioxane, dioxolane, dimethoxyethane, diphenyl ether (diphenyl oxide) or ditolyl ether, and mixtures of these diluents.

**[0081]** The intramolecular Prins reaction is preferably carried out according to the invention in one or more high-boiling diluents (having a boiling point above 220° C., preferably above 240° C., in each case under 1013 mbar), such as diphenyl, diphenyl ether or ditolyl ether or mixtures thereof (such as, for example, "diphyl", a eutectic mixture of 26.5% diphenyl and 73.5% diphenyl oxide, e.g. commercially obtainable under the name Dowtherm® A), since with these diluents, after the reaction has ended it is possible to distil off the lower-boiling reaction products of the formula B (and, where appropriate, unreacted amounts of the educts of the formula A), whereby the catalyst remaining in the distillation bottom product (e.g. the aluminium siloxide of the formula (I)) is not or not noticeably destroyed and in this manner the catalyst solution already employed can be employed for further reaction cycles.

**[0082]** Overall, with the catalysts to be employed according to the invention or according to the invention, a continuous reaction procedure is possible, also on the basis of the comparatively short reaction times of the intramolecular Prins reaction which can be achieved herewith. If a high-boiling diluent is employed in carrying out the intramolecular Prins reaction, the process can be operated overall continuously, for example, by means of adequately known devices, such as a stirred tank or a cascade of stirred tanks and a rectification column. In this context, the reaction mixture is introduced continuously between the rectifying and stripping part of the rectification column, the catalyst together with the high-boiling diluent being obtained in the stripping part and being recycled back to the stirred tank or the cascade of stirred tanks, and it being possible for the desired product of the formula B to be removed in the rectifying part.

**[0083]** If the intramolecular Prins reaction is carried out without a diluent, the addition of a high-boiling diluent (as defined above) before carrying out the distillation is advantageous. In this manner, all the lower-boiling reaction products of the formula B (and, where appropriate, unreacted amounts of the educts of the formula A) can be distilled off, at the same time the stirrability of the distillation bottom product being ensured and the crystallization, precipitation or caking and an (uncontrolled) overheating of the catalyst remaining in the bottom product (in particular an aluminium siloxide of the formula (I)) being avoided.

**[0084]** The catalysts of the formula (I) have a high heat stability. The intramolecular Prins reaction is preferably carried out according to the invention at a temperature in the range of from −10 to 130° C., preferably in the range of from 0 to 60° C., and particularly preferably in the range of 10 to 50° C.

**[0085]** According to the invention, the intramolecular reaction proceeds very rapidly compared with the known catalyst systems, and is regularly concluded within a reaction time of 1-4 hours under the stated reaction conditions (conversion>98%).

**[0086]** The following examples illustrate the invention. Unless stated otherwise, all the data relate to the weight.

EXAMPLE 1

Preparation of Trisarylsilanols of the Formula (IIa) (Applies Accordingly to (IIb), (IIc))

1.1 General Instructions for the Preparation of Trisarylsilanols of the Formula (IIa)

**[0087]** The silanols are prepared in accordance with the methods described in the literature for building up arylsilanes and -silanols.

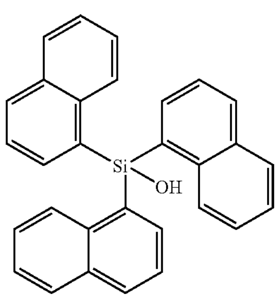
**[0088]** For this, the aryl bromide in question is reacted with the equimolar amount of n-butyllithium in diethyl ether at −20 to 40° C. under an inert gas atmosphere (usually nitrogen or argon). After 5 h and warming to room temperature, approx. 0.33 molar equivalent of a 5 wt. % strength solution of silicon-chloroform (trichlorosilane) $HSiCl_3$ in diethyl ether is added to the reaction mixture. The reaction mixture is then heated under reflux for 3 h.

**[0089]** After cooling, 5 molar equivalents of water are added to the reaction mixture, and the trisarylsilane formed is obtained as a solid.

**[0090]** The trisarylsilane formed in this way is oxidized as an about 10 wt. % strength solution in tetrahydrofuran (THF) with potassium permanganate (regularly 1.5 to 5 molar equivalents) to give the silanol of the formula (IIa). The silanol of the formula (IIa) obtained is then separated off by filtration from the pyrolusite (manganese dioxide) formed. The colourless solution obtained is finally concentrated in vacuo.

**[0091]** The silanol of the formula (IIa) is generally obtained in the form of a white to yellowish solid.

1.2 Preparation of tris(1-naphthyl)silanol




**[0092]** Analogously to Example 1.1, 100 mmol 1-naphthyl bromide were reacted with 100 mmol n-butyllithium (2M solution in cyclohexane). The naphthyllithium formed was then reacted with 33 mmol silicon-chloroform (trichlorosilane) analogously to Example 1.1.

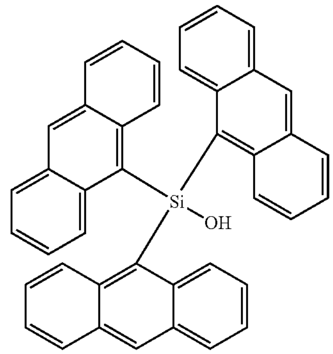
**[0093]** Tris(1-naphthyl)silane was obtained as a white solid in a purity of 99% (GC-MS), yield; 13 g.

**[0094]** As described in Example 1.1, the reaction to give tris(1-naphthyl)silanol was carried out by the oxidation reaction with potassium permanganate.

**[0095]** For this, 9.5 mmol of the tris(1-naphthyl)silane are initially introduced into 100 ml THF. 15 mmol of solid potassium permanganate are then added to the solution and the solution is stirred at room temperature (about 20° C.) for 2 days.

**[0096]** The pyrolusite ($MnO_2$) which forms is separated off by filtration over silica gel. The organic solution of the tris(1-naphthyl)silanol is finally concentrated and the silanol is obtained in the form of a white solid. Yield. 4.04 g (corresponds to 95% of theory),

1.3 Preparation of tris(9-anthracenyl)silanol




**[0097]** Analogously to Example 1.1 for the preparation of tris(9-anthracenyl)silane, 60 mmol 9-anthracenyl bromide were reacted with the equimolar amount of n-butyllithium (2 M solution, 60 mmol) in diethyl ether at −40° C. and the solution was then warmed to ambient temperature (about 20° C.). After cooling the reaction solution to −20° C., this is reacted with 20 mmol silicon-chloroform (trichlorosilane) and the resulting white suspension is then warmed to room temperature. Thereafter, the reaction mixture is heated under reflux for 3 h. After adding 100 g water to the reaction mixture, tris(9-anthracenyl)silane) is filtered off as a yellow solid. Crude yield: 12.3 g, purity; 85.4% (GC-MS). The silane is purified by crystallization from ethanol.

**[0098]** The oxidation of the tris(9-anthracenyl)silane is carried out analogously to Example 1.1 with 5 molar equivalents of potassium permanganate in boiling tetrahydrofuran. The reaction is interrupted after 15 h and, after filtration over silica gel to separate off pyrolusite from the solution, the silanol formed is obtained as a yellowish solid by concentration of the reaction mixture, yield: 10.75 g with a purity of 85% (GC-MS). Further purification is carried out by crystallization from boiling ethanol.

EXAMPLE 2

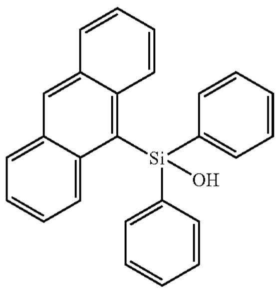
Preparation of Unsymmetrically Substituted Triarylsilanols

2.1 General Instructions for the Preparation of Unsymmetrically Substituted Triarylsilanols of the Formula (IIa), in Particular of Diphenylarylsilanols

**[0099]** For the preparation of unsymmetric triarylsilanols, the lithiumated aryl halide (preferably lithiumated aryl bromide) is reacted with diaryldichlorosilane, e.g. dichlorodiphenylsilane $Ph_2SiCl_2$.

[0100] The aryl bromide employed by way of example is metallized analogously to Example 1.1 with the equimolar amount of n-butyllithium at −40 to −20° C. in diethyl ether and, after warming to ambient tm (approx. 20° C.) is reacted for 5 h with an equimolar amount of the dichlorodiphenylsilane employed by way of example, dissolved in diethyl ether. After warming the reaction solution to ambient temperature, the reaction mixture is heated under reflux for 3 h. Thereafter, for preparation of the silanol water is added to the white suspension formed and the reaction mixture is heated again under reflux for 1 h. The organic phase obtained after separating off the aqueous phase is washed neutral with 5 wt. % strength sodium carbonate solution and concentrated in vacuo. The unsymmetrically substituted triarylsilanols are obtained as white to yellowish solids.

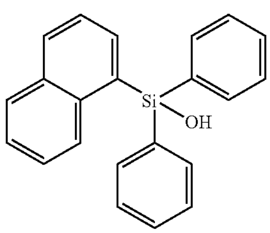
2.2 Preparation of (9-anthracenyl)diphenylsilanol



[0101] For preparation of the silanol, 20 mmol 9-anthracenyl bromide are metallized with the equimolar amount of n-butyllithium (2 M solution in cyclohexane, 20 mmol) at −20° C. and dichlorodiphenylsilane is then added, in accordance with Example 2.1. When the addition of the dichlorodiphenylsilane has ended, the reaction mixture is heated under reflux for 3 h and then hydrolysed by addition of water (100 g).

[0102] After the organic phase which has been separated off has been washed neutral, the solution is concentrated in vacuo and the crude product is obtained as a yellow solid. Crude yield: 5.80 g, content: 69% (GC-MS),

2-3 Preparation of (1-naphthyl)diphenylsilanol



[0103] For preparation of the silanol, 60 mmol 1-naphthyl bromide are metallized with the equimolar amount of n-butyllithium (2 M solution in cyclohexane, 60 mmol) at −20° C. in 400 ml diethyl ether and 60 mmol dichlorodiphenylsilane is then added, in accordance with Example 2.1. After addition of the dichlorodiphenylsilane, the reaction mixture is heated under reflux for 3 h and then hydrolysed by addition of water (100 g). After the organic phase which has been separated off has been washed neutral, the solution is concentrated in vacuo and the crude product is obtained as a white solid. Crude yield: 21.17 g, content: 84% (GC-MS).

## EXAMPLES 3 AND 4

### Preparation of Isopulegol

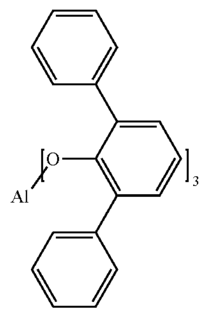
General Instructions for Carrying Out the Cyclization (Intramolecular Prins Reaction)

[0104] The experiments for preparation of isopulegol from citronellal were carried out using anhydrous diluents and under an inert gas atmosphere (nitrogen or argon).

## EXAMPLES 3.1-3.2

### Comparison Example: Preparation of Isopulegol (Analogously to EP 1 225 163 A2, Not According to the Invention)

[0105] 3.1: Preparation of tris(2,6-diphenylphenoxy)aluminium (Catalyst not According to the Invention)



[0106] 3 mmol 2,6-diphenylphenol are initially introduced into toluene under an inert gas. After the 2,6-diphenylphenol has dissolved, 1 mmol triethylaluminium (solution in toluene) is added dropwise to the cooled solution at about 0° C. and the reaction mixture is stirred at room temperature for 1 h. During this procedure, the solution assumes a pale yellowish colour shade, but remains clear.

3.2. Cyclization

[0107] The reaction solution from 3.1 is diluted with 50 ml toluene and cooled to −10° C. 50 mmol of racemic citronellal are added dropwise to the cold reaction solution over a period of 5 minutes.

[0108] Monitoring of the reaction (GC) showed a conversion of 63% after 4 h. Complete conversion was achieved after 20 h, and the selectivity, based on isopulegol and its stereoisomers B2, was 75%, yield: 7.70 g (50 mmol).

## EXAMPLE 3.3

### Comparison Example: Preparation of Isopulegol (Analogously to Synthesis 1978, 147, Not According to the Invention)

[0109] 0.001 mmol zinc bromide is initially introduced into 70 ml toluene under an inert gas. The reaction solution is then temperature-controlled at 85° C. and 0.05 mol citronellal are metered into the reaction solution. The heterogeneous reaction mixture is then stirred at this temperature for 4 h. Thereafter, the reaction mixture is washed with 50 ml 15% strength sodium hydroxide solution and, after washing neutral, the solvent is removed from the reaction mixture under reduced pressure.

[0110] A conversion of 98% was achieved, and the selectivity, based on isopulegol and its stereoisomers B2, was 85%, yield: 50 mmol in the form of a yellow oil.

## EXAMPLES 4-11

### Intramolecular Prins Reaction, According to the Invention, of Citronellal to Give Isopulegol

## EXAMPLE 4

### Use of Two Different Aluminium Siloxide Catalysts

[0111] The cyclization according to the invention of rac-citronellal to isopulegol and its stereoisomers B2 was carried out in the presence of two different aluminium siloxide of the formula (I), and these were prepared in situ starting from either triethylsilanol or tert-butyldimethylsilanol by reaction with an aluminium compound of the formula (III) corresponding to Comparison Example 3.1 (tris(2,6-diphenylphenoxy)aluminium).

[0112] Corresponding to Comparison Example 3.2, 1 mmol of the aluminium siloxide of the formula (I) prepared in situ [$Al(OSiEt_3)_3$ or $Al(OSiMe_2tBu)_3$] was reacted with 50 mmol of citronellal in toluene. The results are shown in the following table, and the data are in GC %.

| Formula (I) | Isopulegol + isomers B2 | Diastereoselectivity for rac-isopulegol rac-B2iso | Conversion |
|---|---|---|---|
| $Al(OSiEt_3)_3$ | 81.2 | 74.8 | 99.1 |
| $Al(OSiMe_2tBu)_3$ | 84.6 | 74.6 | 99.4 |

[0113] At a conversion of >99%, the particular reaction products contained the cyclization products of the intramolecular Prins reaction (isopulegol and isomers B2) to the extent of 81.2% and 84.6 5 respectively, the content of racemic isopulegol rac-B2 iso here being 74.8% and 74.6% respectively, corresponding to a particular content of rac-B2 iso in the reaction products of 60.7% and 63.1% respectively.

## EXAMPLE 5

### Example 5.1

### Preparation of a Catalyst of the Formula (I), $Al(OSiPh_3)_3$

[0114] 1 mmol triethylaluminium (solution in toluene) is added dropwise to a mixture of 3 mmol triphenylsilanol in toluene, after cooling to 0° C. Thereafter, the reaction mixture is warmed to room temperature (approx. 20° C.), the suspension first becoming significantly lighter in colour and then clear. To bring the formation of the aluminium siloxide $Al(OSiPh_3)_3$ of the formula (I) to completion, the reaction mixture is stirred at room temperature for a further 30 min.

### Example 5.2

### Cyclization Reaction

[0115] The reaction mixture from Example 5.1 in toluene is diluted with a further 50 ml toluene and cooled to 0° C. The previously suspended solid is dissolved by the dilution. 50 mmol citronellal are then added dropwise to the resulting solution in the course of 2 min and the reaction mixture is warmed to room temperature. After 3 h, the citronellal is converted completely. The reaction mixture is then washed with 50 ml of 20% strength sodium hydroxide solution and the organic phase obtained is freed from the toluene in vacuo.

[0116] A complete conversion was achieved, and the selectivity, based on isopulegol and its stereoisomers B2, was 100%, yield: 7.70 g (50 mmol) in the form of a pale yellow oil. No Tischtschenko-Claisen products were found.

## EXAMPLE 6

[0117] The aluminium siloxide $Al(OSiPh_3)_3$ was prepared analogously to Example 5.1. The solution containing 1 mmol of the freshly prepared aluminium siloxide was then heated to 40° C. and 100 mmol citronellal as a 50% strength solution in toluene were added dropwise. When the metering in had ended, the reaction mixture was stirred at 40° C. for a further 4 h and the reaction was then interrupted by addition of 50 ml 15% strength sodium hydroxide solution. After washing neutral and distilling off the solvent, the reaction product B2 was obtained as a colourless oil, yield: 14.8 g.

[0118] A conversion of 99% was achieved, and the selectivity, based on isopulegol and its stereoisomers B2, was >99.5%. No Tischtschenko-Claisen products were found.

## EXAMPLE 7

[0119] The aluminium siloxide $Al(OSiPh_3a$ was prepared analogously to Example 5.1. The solution containing 1 mmol of the freshly prepared aluminium siloxide was then heated to 60° C. and 100 mmol citronellal as a 50% strength solution in toluene were added dropwise. When the metering in had ended, the reaction mixture was stirred at 60° C. for a further 2 h and the reaction was then interrupted by addition of 50 ml 15% strength sodium hydroxide solution. After washing neutral and distilling off the solvent, the reaction product B2 was obtained as a colourless oil, yield: 14.8 g.

[0120] A conversion of 98% was achieved, and the selectivity, based on isopulegol and its stereoisomers B2, was 98%. No Tischtschenko-Claisen products were found.

## EXAMPLE 8

[0121] The aluminium siloxide $Al(OSiPh_3)_3$ was prepared analogously to Example 2a. The solution containing 1 mmol of the freshly prepared aluminium siloxide was then heated to 40° C. and 200 mmol citronellal as a 50% strength solution in toluene were added dropwise in the course of 30 min. When the metering in had ended, the reaction mixture was stirred at 40° C. for a further 4 h and the reaction was then interrupted by addition of 20% strength sodium hydroxide solution. After washing neutral and distilling off the solvent, the reaction product B2 was obtained as a colourless oil, yield: 30.0 g. A conversion of 97% was achieved, and the selectivity, based on isopulegol and its stereoisomers B2, was >99.5%. No Tischtschenko-Claisen products were found.

## EXAMPLE 9

### Re-Use of the tris(triphenylsilyloxy)aluminium Catalyst $Al(OSiPh_3)_3$ for the Preparation of i-Isopulegol from d-Citronellal

[0122] 5 mmol triethylaluminium as a solution are added dropwise to a suspension of 15 mmol triphenylsilanol in ditolyl ether as a high-boiling diluent, after cooling to 0° C.

Thereafter, the reaction mixture was warmed to room temperature (approx. 20° C.). To bring the formation of the aluminium siloxide $Al(OSiPh_3)_3$ of the formula (I) to completion, the reaction mixture was stirred at room temperature for a further 45 min. 250 mmol d-citronellal were added to this mixture at 0° C. and the mixture was warmed to room temperature. After 3 h, complete conversion of the citronellal is achieved.

**[0123]** l-isopulegol and its stereoisomers B2 were then separated off completely from the high-boiling diluent by distillation under a vacuum of 1-3 mbar to a bottom temperature of 125° C.

**[0124]** After cooling of the mixture remaining in the bottom of the distillation, which chiefly comprised ditolyl ether and aluminium siloxide $Al(OSiPh_3)_3$, this was cooled to 0° C. and 250 mmol d-citronellal were again added. Complete conversion was in turn observed after 3 h.

**[0125]** Further repetitions were carried out by the procedure described above. The results are summarized in the following table.

| Run no. | i-Isopulegol + isomers B2 | Diastereoselectivity for I-isopulegol B2iso | Conversion |
|---|---|---|---|
| 1 | 100 | 76.3 | 100 |
| 2 | 100 | 73.9 | 99.5 |
| 3 | 100 | 77.1 | 99.5 |
| 4 | 100 | 77.5 | 99.8 |
| 5 | 100 | 77.8 | 99.7 |
| 6 | 100 | 77.7 | 99.7 |

**[0126]** The particular reaction products comprised the cyclization products of the intramolecular Prins reaction (1-isopulegol and isomers B2) and, where appropriate, unreacted d-citronellal (up to 0.5%).

**[0127]** The content of 1-isopulegol B2 iso in the cyclization products of the intramolecular Prins reaction (1-isopulegol and isomers B2) in the particular run was in the range of from 73.9% to 77.8%, corresponding to a particular content of B2 iso in the particular reaction products of 73.5% (run no. 2) to 77.6% (run no. 5).

## EXAMPLE 10

**[0128]** The preparation of the aluminium siloxide $Al(OSi(1\text{-naphthyl})_3)_3$ was carried out in situ analogously to Example 5.1 from 3 mmol tris(1-naphthyl)silanol and 1 mmol triethylaluminium. 100 mmol d-citronellal were added dropwise to the freshly prepared catalyst at 0° C. and the reaction mixture was warmed to room temperature. When the metering in had ended, the reaction mixture was stirred at room temperature (approx. 20° C.) for a further 4 h and the reaction was then interrupted by addition of 50 ml 15% strength sodium hydroxide solution. After washing neutral and distilling off the solvent, the reaction product B2 was obtained as a colourless oil, yield: 14.8 g.

**[0129]** A conversion of 99% was achieved, and the selectivity, based on 1-isopulegol and its stereoisomers B2, was 100%. No Tischtschenko-Claisen products were found. The diastereoselectivity of the intramolecular Prins reaction for 1-isopulegol B2 iso was 96.5%, corresponding to a diastereomer excess of de 93%.

## EXAMPLE 11

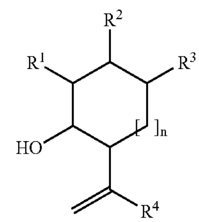
**[0130]** The preparation of the aluminium siloxide $Al(OSi(1\text{-naphthyl})Ph_2)_3$ was carried out in situ analogously to Example 5.1 from 3 mmol 1-naphthyldiphenylsilanol and 1 mmol triethylaluminium. At 0° C., 100 mol d-citronellal were added dropwise to the freshly prepared catalyst at 0° C. and the reaction mixture was warmed to room temperature. When the metering in had ended, the reaction mixture was stirred at room temperature (approx. 20° C.) for a further 4 h and the reaction was then interrupted by addition of 50 ml 15% strength sodium hydroxide solution. After washing neutral and distilling off the solvent, the reaction product B2 was obtained as a colourless oil, yield: 14.8 g.

**[0131]** A conversion of 99% was achieved, and the selectivity, based on isopulegol and its stereoisomers B2, was >99,5%. No Tischtschenko-Claisen products were found. The diastereoselectivity for 1-isopulegol B2 iso was 80%.

**1-17**. (canceled)

**18**. A process for the preparation of a compound of the formula B

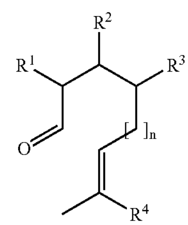
B



comprising:

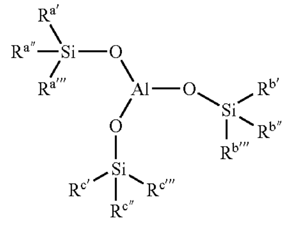
providing a compound of the formula A

A



reacting the compound of the formula A in an intramolecular reaction in the presence of an aluminium siloxide of the formula (I)

(I)



wherein $R^1$, $R^2$, $R^3$ in each case independently of one another are hydrogen or methyl, $R^4$ is hydrogen or an alkyl radical having 1 to 6 C atoms, and n is 0, 1 or 2

and wherein $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are hydrogen or an organic radical, with the proviso that at least one of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime}$ and one of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$ and one of the radicals $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ is not hydrogen; and

independently of one another also two or three of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, two or three of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$ and two or three of the radicals $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ can be covalently bonded to one another.

**19**. The process of claim **18**, wherein:

$R^1$ and $R^2$ in each case independently of one another are hydrogen or methyl,

$R^3$ is hydrogen,

$R^4$ is methyl, and

n is 0 or 1.

**20**. The process of claim **18**, wherein the compound of the formula A is chosen from the group consisting of 2,6-dimethyl-5-heptenal and citronellal (3,7-dimethyl-6-octenal).

**21**. The process of claim **18**, wherein the aluminium siloxide of the formula (I) is prepared in situ and/or is freshly prepared.

**22**. The process of claim **18**, wherein the intramolecular reaction of the compound of the formula A is carried out in a diluent, the boiling point of which is higher than that of the compounds of the formulae A and B; or

after the intramolecular reaction of the compound of the formula A has taken place, a diluent, the boiling point of which is higher than that of the compounds of the formulae A and B, is added,

said process further comprising:

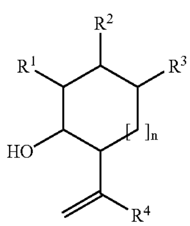
separating off, by distillation, the compound of the formula B from the diluent and the aluminium siloxide of the formula (I).

**23**. The process of claim **18**, further comprising

recycling the aluminium siloxide of the formula (I) in the intramolecular reaction of the compound of the formula A.

**24**. A process for the preparation of a compound of the formula B

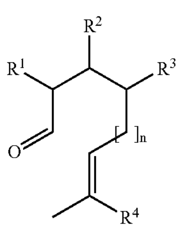
B



comprising:

providing a compound of the formula A

A



mixing and/or reacting

either an aluminium compound of the formula (III)

$$H_pAl(R^5)_{3-p} \quad \text{(III)}$$

wherein $R^5$ is an alkyl radical having 1 to 4 C atoms or an aryl radical and

p is 0, 1 or 2;

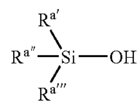
or an aluminium compound of the formula (IV)

$$MAlH_4 \quad \text{(IV)}$$

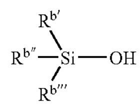
wherein M is lithium, sodium or potassium;

with silanols of the formulae (IIa), (IIb) and (IIc),

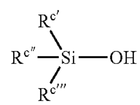
(IIa)



(IIb)



(IIc)



which can be identical or different,

wherein $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$, $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$, independently of one another are hydrogen or an organic radical, with the proviso that at least one of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$ and one of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$ and one of the radicals $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$, is not hydrogen,

wherein independently of one another also two or three of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, two or three of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b}$ and two or three of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, can be covalently bonded to one another; and

reacting the compound of the formula A in an intramolecular reaction in the presence of the mixture and/or the reaction product of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc).

**25**. The process of claim **24**, wherein the reaction production of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc) is prepared in situ and/or is freshly prepared.

**26**. The process of claim **24**, wherein the intramolecular reaction of the compound of the formula A is carried out in a diluent, the boiling point of which is higher than that of the compounds of the formulae A and B; or

after the intramolecular reaction of the compound of the formula A has taken place, a diluent, the boiling point of which is higher than that of the compounds of the formulae A and B, is added,

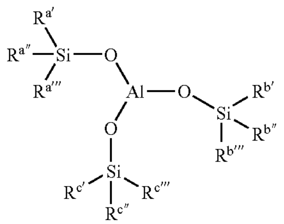
said process further comprising:

separating off, by distillation, the compound of the formula B from the diluent and the reaction product of the reaction of the aluminium compound (III) or (IV) with the silanols (IIa), (IIb) and (IIc).

**27**. A process comprising undergoing a chemical reaction in the presence of a catalyst selected from the group consisting of

an aluminium siloxide of the formula (I)

(I)



and

a mixture and/or a reaction product of a reaction either of an aluminium compound of the formula (III)

$$H_pAl(R^5)_{3-p} \qquad (III)$$

wherein

$R^5$ is an alkyl radical having 1 to 4 C atoms or an aryl radical and

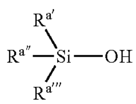
p is 0, 1 or 2,

or of an aluminium compound of the formula (IV)

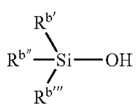
$$MAlH_4 \qquad (IV)$$

wherein M is chosen from lithium, sodium or potassium; with silanols of the formulae (IIa), (IIb) and (IIc),

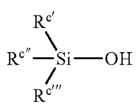
(IIa)



(IIb)



(IIc)



which can be identical or different,

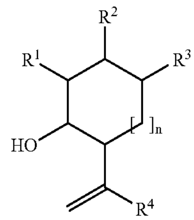
wherein $R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are hydrogen or an organic radical, with the proviso that at least one of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$ and one of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and one of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ is not hydrogen, and

wherein independently of one another also two or three of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, two or three of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and two or three of the radicals $R^{c'}$; $R^{c''}$, $R^{c''}$ can be covalently bonded to one another.

**28**. The process of claim **27**, wherein the reaction is an intramolecular Prins reaction.

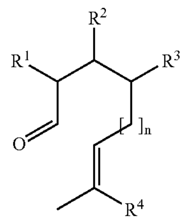
**29**. The process of claim **27**, wherein the chemical reaction produces a compound of the formula B

B



from a compound of the formula A

A



wherein in the formulae A and B, $R^1$, $R^2$, $R^3$ and n in each case have the same meaning and

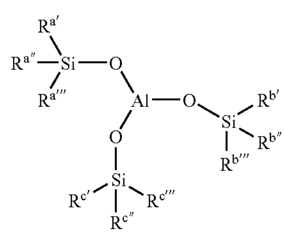
$R^1$, $R^2$, $R^3$ in each case independently of one another are hydrogen or methyl, $R^4$ is hydrogen or an alkyl radical having 1 to 6 C atoms, and n is 0, 1 or 2.

**30**. The process of claim **18**, wherein

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are an optionally substituted radical chosen from the group consisting of $C_1$-$C_{20}$-alkyl, $C_1$-$C_{20}$-heteroalkyl, $C_3$-$C_{20}$-cycloalkyl, $C_4$-$C_{20}$-cycloalkylalkyl, $C_2$-$C_{20}$-alkenyl, $C_3$-$C_{20}$-cycloalkenyl, $C_4$-$C_{20}$-cycloalkenylalkyl, $C_2$-$C_{20}$-alkynyl, $C_5$-$C_{20}$-cycloalkylalkynyl, $C_1$-$C_{20}$-alkoxy, $C_3$-$C_{20}$-cycloalkoxy, $C_1$-$C_{20}$-cycloalkylalkoxy, $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_2$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_9$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl; and wherein independently of one another also two or three of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, two or three of the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ and two or three of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ may be covalently bonded to one another.

**31**. An aluminium siloxide of the formula (I)

(I)



wherein:

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are an optionally substituted radical chosen from the group consisting of $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{25}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_8$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_9$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl,

excluding the compound $Al(OSiPh_3)_3$.

**32**. A mixture

either of an aluminium compound of the formula (III)

$$H_pAl(R^5)_{3-p} \quad \text{(III)}$$

wherein $R^5$ is an alkyl radical having 1 to 4 C atoms or an aryl radical and

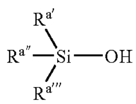
p is 0, 1 or 2;

or of an aluminium compound of the formula (IV)

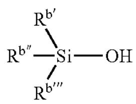
$$MAlH_4 \quad \text{(IV)}$$

wherein M is chosen from lithium, sodium or potassium, with silanols of the formulae (IIa), (IIb) and (IIc),

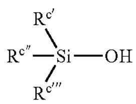
(IIa)



(IIb)



(IIc)



which can be identical or different,

wherein in the formulae (IIa), (IIb) and (IIc):

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are an optionally substituted radical chosen from the groups consisting of $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{25}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_8$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl,

wherein the compound comprises no $AlMe_3$ and/or $HOSiPh_3$.

**33**. A reaction product of a reaction

either of an aluminium compound of the formula (III)

$$H_pAl(R^5)_{3-p} \quad \text{(III)}$$

wherein $R^5$ is an alkyl radical having 1 to 4 C atoms or an aryl radical and

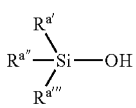
p is 0, 1 or 2;

or of an aluminium compound of the formula (IV)

$$MAlH_4 \quad \text{(IV)}$$

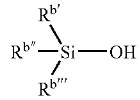
wherein M is chosen from lithium, sodium or potassium, with silanols of the formulae (IIa), (IIb) and (IIc),

(IIa)

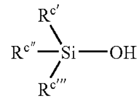


-continued

(IIb)



(IIc)



which can be identical or different,

wherein in the formulae (IIa), (IIb) and (IIc):

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are an optionally substituted radical chosen from the group consisting of $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{25}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_8$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl,

excluding the compound $Al(OSiPh_3)_3$.

**34**. The aluminium siloxide of claim **31**, wherein:

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are an optionally substituted radical chosen from the group consisting of $C_6$-$C_{20}$-aryl, $C_3$-$C_{20}$-heteroaryl, $C_7$-$C_{20}$-arylalkyl, $C_8$-$C_{20}$-cycloalkylaryl, $C_9$-$C_{20}$-cycloalkenylaryl, $C_6$-$C_{20}$-cycloalkylheteroaryl, $C_9$-$C_{20}$-heterocycloalkylaryl, $C_9$-$C_{20}$-heterocycloalkenylaryl, $C_8$-$C_{20}$-heterocycloalkenylheteroaryl and $C_4$-$C_{20}$-heteroarylalkyl.

**35**. The aluminium siloxide of claim **31**, wherein:

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are an optionally substituted radical chosen from the group consisting of $C_6$-$C_{20}$-aryl, $C_3$-$C_{20}$-heteroaryl, $C_8$-$C_{20}$-cycloalkylaryl, $C_9$-$C_{20}$-cycloalkenylaryl, $C_7$-$C_{20}$-cycloalkylheteroaryl, $C_8$-$C_{20}$-heterocycloalkylaryl, $C_8$-$C_{20}$-heterocycloalkenylaryl and $C_8$-$C_{20}$-heterocycloalkenylheteroaryl.

**36**. The process of claim **18**, wherein, for the aluminium siloxide of the formula (I) and the silanols of the formulae (IIa), (IIb) and (IIc):

the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$ are identical, the radicals $R^{b'}$, $R^{b''}$, $R^{b'''}$ are identical and the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ are identical.

**37**. The process of claim **24**, wherein

$R^{a'}$, $R^{a''}$, $R^{a'''}$, $R^{b'}$, $R^{b''}$, $R^{b'''}$, $R^{c'}$, $R^{c''}$, $R^{c'''}$ independently of one another are an optionally substituted radical chosen from the group consisting of $C_1$-$C_{20}$-alkyl, $C_1$-$C_{20}$-heteroalkyl, $C_3$-$C_{20}$-cycloalkyl, $C_4$-$C_{20}$-cycloalkylalkyl, $C_2$-$C_{20}$-alkenyl, $C_3$-$C_{20}$-cycloalkenyl, $C_4$-$C_{20}$-cycloalkenylalkyl, $C_2$-$C_{20}$-alkynyl, $C_5$-$C_{20}$-cycloalkylalkynyl, $C_1$-$C_{20}$-alkoxy, $C_3$-$C_{20}$-cycloalkoxy, $C_5$-$C_{20}$-cycloalkylalkoxy, $C_3$-$C_{25}$-aryl, $C_2$-$C_{25}$-heteroaryl, $C_4$-$C_{25}$-arylalkyl, $C_8$-$C_{25}$-cycloalkylaryl, $C_9$-$C_{25}$-cycloalkenylaryl, $C_5$-$C_{25}$-cycloalkylheteroaryl, $C_8$-$C_{25}$-heterocycloalkylaryl, $C_8$-$C_{25}$-heterocycloalkenylaryl, $C_8$-$C_{25}$-heterocycloalkenylheteroaryl and $C_3$-$C_{25}$-heteroarylalkyl; and wherein independently of one another also two or three of the radicals $R^{a'}$, $R^{a''}$, $R^{a'''}$, two or three of the radicals $R^{b'}$, $R^{b''}$, $R^{b''}$ and two or three of the radicals $R^{c'}$, $R^{c''}$, $R^{c'''}$ may be covalently bonded to one another.

**38**. The process of claim **18**, wherein in formula (I)

$R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$, $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ independently of one another are hydrogen or an optionally substituted radical chosen from the group consisting of alkyl, heteroalkyl, cycloalkyl, cycloalkylalkyl, alkenyl, cycloalkenyl, cycloalkenylalkyl, alkynyl, cycloalkylalkynyl, alkoxy, cycloalkoxy, cycloalkylalkoxy, aryl, heteroaryl, arylalkyl, cycloalkylaryl, cycloalkenylaryl, cycloalkylheteroaryl, heterocycloalkylaryl, heterocycloalkenylaryl, heterocycloalkenylheteroaryl and heteroarylalkyl, with the proviso that at least one of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$ and one of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$ and one of the radicals $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ is not hydrogen;

wherein independently of one another also two or three of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, two or three of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$ and two or three of the radicals $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ can be covalently bonded to one another.

**39**. The process of claim **24**, wherein $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$, $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ independent of one another are hydrogen or an optionally substituted radical chosen from the group consisting of alkyl, heteroalkyl, cycloalkyl, cycloalkylalkyl, alkenyl, cycloalkenyl, cycloalkenylalkyl, alkynyl, cycloalkylalkynyl, alkoxy, cycloalkoxy, cycloalkylalkoxy, aryl, heteroaryl, arylalkyl, cycloalkylaryl, cycloalkenylaryl, cycloalkylheteroaryl, heterocycloalkylaryl, heterocycloalkenylaryl, heterocycloalkenylheteroaryl and heteroarylalkyl, with the proviso that at least one of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$ and one of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$ and one of the radicals $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ is not hydrogen,

wherein independently of one another also two or three of the radicals $R^{a\prime}$, $R^{a\prime\prime}$, $R^{a\prime\prime\prime}$, two or three of the radicals $R^{b\prime}$, $R^{b\prime\prime}$, $R^{b\prime\prime\prime}$ and two or three of the radicals $R^{c\prime}$, $R^{c\prime\prime}$, $R^{c\prime\prime\prime}$ can be covalently bonded to one another.

**40**. The process of claim **24**, wherein

$R^1$ and $R^2$ in each case independently of one another are hydrogen or methyl,

$R^3$ is hydrogen,

$R^4$ is methyl, and

n is 0 or 1.

* * * * *