Title: PROCESSES FOR THE HYDROGENATION OF α,β-UNSATURATED KETONES

Abstract: The catalytic hydrogenation of α,β-unsaturated ketones R²=CH=CH-CO-R² in which R¹ and R² independently of one another represent straight-chain or branched C₃-C₁₂-alkyl or C₃-C₁₂-hydroxyalkyl, straight-chain or branched C₃-C₁₂-alkenyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkenyl, C₊-C₁₄-aryl or C₆-C₁₄-aryl, where at least one of R¹ and R² is monosubstituted to trisubstituted by halogen, to give the respective saturated ketones R¹=CH₂-CH₂-CO-R² in which R¹ and R² assume the meaning of R¹ and R² with the exception that alkyl and cycloalkenyl are hydrogenated to the respective alkyl or cycloalkyl, wherein the hydrogenation process comprises combining the α,β-unsaturated ketones and a reaction medium comprising water or alcohol in amounts such that the wt% of the α,β-unsaturated ketones based on the total weight of the α,β-unsaturated ketones and the reaction medium is at least about 60 wt%, and the hydrogenation is carried out in the presence of at least (i) an organic amine, (ii) a Ni-containing catalyst, and (iii) an organic sulphur compound.
PROCESSES FOR THE HYDROGENATION OF \(\alpha,\beta\)-UNSATURATED KETONES

BACKGROUND

[0001] US Patent 4,940,819 describes a process for the catalytic hydrogenation of \(\alpha,\beta\)-unsaturated ketones \(R^1-\text{CH}==\text{CH}-\text{CO}-R^2\) in which \(R^1\) and \(R^2\) independently of one another represent straight-chain or branched \(C_1-C_{12}\)-alkyl or \(C_2-C_{12}\)-hydroxyalkyl, straight-chain or branched \(C_2-C_{12}\)-alkenyl, \(C_3-C_{3}\)-cycloalkyl, \(C_3-C_{8}\)-cycloalkenyl, \(C_7-C_{14}\)-aralkyl or \(C_6-C_{12}\)-aryl, where at least one of \(R^1\) and \(R^2\) is monosubstituted to trisubstituted by halogen, to give the respective saturated ketones \(R^{11}==\text{CH}_2-\text{CH}_2-\text{CO}-R^{12}\) in which \(R^{11}\) and \(R^{12}\) assume the meaning of \(R^1\) and \(R^2\) with the exception that alkenyl and cycloalkenyl are hydrogenated to the respective alkyl or cycloalkyl, which is characterized in that a Ni-containing catalyst is employed and that the reaction is carried out in the presence of an organic sulphur compound \(R^3-S(=O)n-R^4\) in which \(R^3\) and \(R^4\) independently of one another denote straight-chain or branched \(C_1-C_{12}\)-alkyl, hydroxy-\(C_2-C_{12}\)-alkyl, carboxy-\(C_1-C_{12}\)-alkyl or phenyl, and furthermore \(R^3\) and \(R^4\) may together represent \(\text{CH}==\text{CH}==\text{CH}==\cdot, \cdot\text{(CH}_2\text{)}_4\cdot\cdot\), \(\cdot\text{CH}_2\text{O}\cdot\cdot\), \(\cdot\text{(CH}_2\text{)}_2\text{S}\cdot\cdot\text{(CH}_2\text{)}_2\cdot\cdot\) or \(\cdot\text{(CH}_2\text{)}_2\text{O}\cdot\cdot\text{(CH}_2\text{)}_2\cdot\cdot\). \(R^4\) may additionally denote hydrogen or CO-\(C_1-C_{12}\)-alkyl and \(n\) assumes the value 0 or 1. It is disclosed that the reaction medium employed can be alcohols, such as methanol, ethanol, isopropanol, butanol, aliphatic or aromatic hydrocarbons, such as toluene, xylene, cyclohexane, iso-octane and the like, ethers, such as tetrahydrofuran, dioxane or methyl tert-butyl ether, esters, such as ethyl acetate and lastly the reaction product itself if it is liquid at the reaction temperature; and, further that a proportion of water (for example up to 20% by weight of the total reaction medium) does not interfere, particularly if the reaction medium is water-soluble. It is also disclosed that in a preferred variant, the process is carried out by the addition of a basic substance at a pH of 8 – 14. Numerous basic substances are disclosed, including basic substances that comprise organic amine and those that do not comprise organic amine.

[0002] In the examples provided in US Patent 4,940,819, the weight percent of the Ni-containing catalyst as to the total weight of the catalyst and the \(\alpha,\beta\)-unsaturated ketones to be hydrogenated ranges from about 4 wt% (5.6 g of Ni-containing catalyst; 139 g of \(\alpha,\beta\)-unsaturated ketone) to about 14 wt% (10 g of Ni-containing catalyst; 63 g of \(\alpha,\beta\)-unsaturated ketone).
In the examples provided in US Patent 4,940,819, the weight percent of the organic sulphur compound as to the total weight of the organic sulphur compound and the \( \alpha,\beta \)-unsaturated ketones to be hydrogenated ranges from about 0.01 wt% (0.015 g of organic sulphur compound; 120 g of \( \alpha,\beta \)-unsaturated ketone) to about 0.71 wt% (0.45 g of organic sulphur compound; 63 g of \( \alpha,\beta \)-unsaturated ketone). However, no basic substance is used in the examples, except that a basic substance that does not comprise organic amine is used in examples in which the weight percent of the organic sulphur compound as to the total weight of the organic sulphur compound and the \( \alpha,\beta \)-unsaturated ketones to be hydrogenated is about 0.50 wt% (0.7 g of organic sulphur compound; 139 g of \( \alpha,\beta \)-unsaturated ketone).

In the examples provided in US Patent 4,940,819, the weight percent of the \( \alpha,\beta \)-unsaturated ketones to be hydrogenated as to the total weight of the ketones and the reaction medium ranges from about 17 wt% (63 g of ketones; 300 g of tetrahydrofuran) to about 40 wt% (120 g of ketones; 180 g of methanol).

In spite of the disclosure of US 4,940,819, and other known processes for the catalytic hydrogenation of \( \alpha,\beta \)-unsaturated ketones, a need remains for such processes that accommodate a higher percentage weight throughput of ketones per total weight of the ketones and the reaction medium and provide additional commercial advantages, such as allowing a reduction in the amount of raw materials required.

**THE INVENTION**

This invention meets the above-described need by providing processes for the catalytic hydrogenation of \( \alpha,\beta \)-unsaturated ketones \( \text{R}^1\text{CH}═\text{CH}\text{CO─R}^2 \) in which \( \text{R}^1 \) and \( \text{R}^2 \) independently of one another represent straight-chain or branched \( \text{C}_1\text{─C}_{12}\text{─alkyl} \) or \( \text{C}_2\text{─C}_{12}\text{─hydroxyalkyl}, \) straight-chain or branched \( \text{C}_2\text{─C}_{12}\text{─alkenyl}, \) \( \text{C}_3\text{─C}_8\text{─cycloalkyl}, \) \( \text{C}_3\text{─C}_6\text{─cycloalkenyl}, \) \( \text{C}_7\text{─C}_{14}\text{─aralkyl} \) or \( \text{C}_6\text{─C}_{12}\text{─aryl}, \) where at least one of \( \text{R}^1 \) and \( \text{R}^2 \) is monosubstituted to trisubstituted by halogen, to give the respective saturated ketones \( \text{R}^{11}\text{─CH}_2\text{─CH}_2\text{─CO─R}^{12} \) in which \( \text{R}^{11} \) and \( \text{R}^{12} \) assume the meaning of \( \text{R}^1 \) and \( \text{R}^2 \) with the exception that alkenyl and cycloalkenyl are hydrogenated to the respective alkyl or cycloalkyl, which is characterized in that the process comprises combining at least the \( \alpha,\beta \)-unsaturated ketones and a reaction medium comprising alcohol or water, and the hydrogenation is carried out in the presence of at least (i) an organic amine, (ii) a Ni-containing catalyst, and (iii) an organic sulphur compound \( \text{R}^3\text{─S(═O)}_n\text{─R}^4 \) in which \( \text{R}^3 \) and \( \text{R}^4 \) independently of one another denote straight-chain or branched.
C_{1-12}-alkyl, hydroxy-C_{2-12}-alkyl, carboxy-C_{1-12}-alkyl or phenyl, and furthermore R^3 and R^4 may together represent -CH=CH_2=-CH=-CH_2=, -(CH_2)_n=-, -(CH_2)_n=, -(CH_2)_2=S-(CH_2)_2= or -(CH_2)_2-O-(CH_2)_2=, R^4 may additionally denote hydrogen or CO-C_{1-12}-alkyl and n assumes the value 0 or 1, in amounts such that the wt% of the organic sulphur compound based on the total weight of the organic sulphur compound and the α,β-unsaturated ketones is less than about 0.50 wt% and/or in amounts such that the wt% of the Ni-containing catalyst based on the total weight of the Ni-containing catalyst and the α,β-unsaturated ketones is less than about 4 wt%. The α,β-unsaturated ketones and the reaction medium can be combined in amounts such that the wt% of the α,β-unsaturated ketones based on the total weight of the α,β-unsaturated ketones and the reaction medium is at least about 60 wt%.

[0007] We have discovered that by using an organic amine and a reaction medium comprising alcohol or water, the initial weight percent of the α,β-unsaturated ketones to be hydrogenated as to the total weight of the α,β-unsaturated ketones and the reaction medium can be about 60 wt% and greater, thus providing an advantageously high throughput without undesirable side reactions, such as the retro-Aldol reaction we observed when a basic substance not comprising organic amine was used. In processes according to this invention, the primary purpose of the reaction medium is to adjust the polarity of the reaction composition. Processes according to this invention can be conducted neat, i.e., in the absence of the reaction medium. We have also discovered that by using an organic amine and a reaction medium comprising alcohol or water, starting amounts of Ni-containing catalyst and organic sulphur compound can be reduced substantially as compared to current processes. A benefit, in addition to reduction in raw material costs, is reduction in waste disposal costs.

[0008] As will be familiar to those skilled in the art, the terms "combined" and "combining" as used herein mean that the components that are "combined" or that one is "combining" are put into a container with each other. Likewise a "combination" of components means the components having been put together in a container. This invention also provides such compositions and methods wherein the composition is an activator composition.

[0009] This invention is described in connection with specific embodiments. It is understood that this invention is not limited to any one of these specific embodiments.
\(\alpha, \beta\)-Unsaturated Ketones

\[0010\] \(\alpha, \beta\)-unsaturated ketones suitable for hydrogenating according to this invention include \(\alpha, \beta\)-unsaturated ketones \(R^1-CH=CH-CO-R^2\) in which \(R^1\) and \(R^2\) independently of one another represent straight-chain or branched \(C_1-C_{12}\)-alkyl or \(C_2-C_{12}\)-hydroxyalkyl, straight-chain or branched \(C_2-C_{12}\)-alkenyl, \(C_3-C_8\)-cycloalkyl, \(C_3-C_8\)-cycloalkenyl, \(C_7-C_{14}\)-aralkyl or \(C_6-C_{12}\)-aryl, where at least one of \(R^1\) and \(R^2\) is monosubstituted to trisubstituted by halogen.

\[0011\] Straight-chain or branched \(C_1-C_{12}\)-alkyl can be, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, amyl, hexyl, octyl, decyl or dodecyl; \(C_1-C_6\)-alkyl and \(C_1-C_4\)-alkyl are included. Hydroxyalkyl carries a hydroxyl group in any position, for example in the \(\omega\)-position, and may furthermore be interrupted in the carbon chain by ether oxygen. Carboxy-alkyl carries a carboxyl group in any position, e.g., in the \(\alpha\)- or \(\omega\)-position. Carboxy-alkyl can be \(C_1-C_{12}\)-alkyl; \(C_1-C_6\)-alkyl and \(C_1-C_4\)-alkyl are included.

\[0012\] Straight-chain or branched \(C_2-C_{12}\)-alkenyl can be, for example, vinyl, propenyl, butenyl, isobutenyl, pentenyl, hexenyl, octenyl, decenyl or dodecenyl; \(C_2-C_6\)-alkenyl and \(C_2-C_4\)-alkenyl are included.

\[0013\] \(C_3-C_8\)-cycloalkyl can be, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl, any of which can be substituted by one or two methyl or ethyl groups; substituted or unsubstituted cyclopropyl, cyclopentyl or cyclohexyl are included.

\[0014\] \(C_3-C_8\)-cycloalkenyl can be, for example, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cycloheptenyl or cyclooctenyl.

\[0015\] \(C_7-C_{14}\)-aralkyl can be, for example, benzyl, phenylethyl, naphthylmethyl, naphthylethyl, biphenyl-methyl or biphenyl-ethyl.

\[0016\] \(C_6-C_{12}\)-aryl can be, for example, phenyl, e.g., 4-chlorophenyl, or naphthyl or biphenyl.

\[0017\] At least one of \(R^1\) and \(R^2\) in the \(\alpha, \beta\)-unsaturated ketone is monosubstituted to trisubstituted by halogen, such as fluorine, chlorine or bromine. In the case of multiple substitution, it is not required that each substitution be by the same type of halogen atom. For example, one substitution can be by fluorine and a second substitution by bromine.

\[0018\] Each \(R^1\) or \(R^2\) that is aromatic can furthermore carry one or two methyl or ethyl groups, or methoxy or ethoxy groups, and also the hydroxyl group.
α,β-unsaturated ketones R₁─CH═CH─CO─R² can be used in which R¹ and R² independently of one another denote straight-chain or branched C₁–C₆-alkyl, C₂–C₆-alkenyl, cyclopropyl, cyclopentyl, cyclohexyl, benzyl, phenylethyl or phenyl, where at least one of R¹ and R² represents phenyl and where furthermore at least one of R¹ and R² is monosubstituted to trisubstituted by halogen.

Further suitable α,β-unsaturated ketones are R¹─CH═CH─CO─R² in which R¹ denotes phenyl and R² denotes straight-chain or branched C₁–C₆-alkyl, C₂–C₆-alkenyl, cyclopropyl, benzyl or phenyl, where at least one of R¹ and R² is monosubstituted to trisubstituted by halogen.

Further ketones are 5-halophenyl-2,2-dimethylpent-4-en-3-ones, particularly 5-(4-chlorophenyl)-2,2-dimethylpent-4-en-3-one, and 6-halophenyl-3,3-dimethylhex-5-en-4-ones.

All α,β-unsaturated ketones are in each case distinguished by at least one substituent which is substituted by halogen.

The α,β-unsaturated ketones to be used can be prepared via aldol condensation, as will be familiar to those skilled in the art.

Alcohol

Alcohol used can be any suitable alcohol or mixture of alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, sec butanol and/or mixtures comprising methanol, ethanol, propanol, isopropanol, butanol, or sec butanol.

Water

Water used in processes of this invention can be from any suitable source of potable water.

Reaction Medium

The reaction medium used in processes of this invention can comprise alcohol or water, which includes mixtures thereof. The reaction medium can comprise at least about 50% alcohol up to about 100% alcohol. The reaction medium can consist essentially of alcohol. The reaction medium can comprise at least about 50% water up to about 100% water. The reaction medium can consist essentially of water. The reaction medium can comprise alcohol and water.
Organic Amine

[0027] Organic amines suitable for use in processes of this invention include aliphatic amines, e.g., triethylamine or tripropylamine, and heterocyclic amines. The organic amine(s), if water-soluble, may be used in aqueous solution form or in solid form.

Ni–Containing Catalysts

[0028] Catalysts used according to this invention can be Ni–containing, such as Ni on supports, Ni in the form of elemental nickel sponge, Ni oxide, Raney nickel and others. Supports can be, for example, SiO₂, Al₂O₃, pumice, carbon and other supports known to those skilled in the art. However, Raney catalysts, such as Raney nickel, Raney nickel–iron, Raney nickel–cobalt or Raney nickel–iron–cobalt in anhydrous or even water-moist or reaction medium/solvent-moist form can be used.

Organic Sulphur Compounds

[0029] Processes according to this invention can be carried out in the presence of one or more organic sulphur compounds \( R^{13} = S(=O)_{n} = R^{14} \), where \( R^{13} \) and \( R^{14} \) independently of one another denote alkyl, hydroxy–\( C_{2}−C_{12}− \)alkyl or carboxy–\( C_{1}−C_{12}− \)alkyl, and where \( R^{14} \) additionally may denote CO–\( C_{1}−C_{6}− \)alkyl and \( n \) assumes the value 0 or 1.

[0030] Examples of such compounds are bis-(2-hydroxyethyl) sulphide, bis-(2-hydroxypropyl) sulphide, thiadicetic acid and its alkali metal salts, thioanisole, thiodipropionic acid, its salts and its dimethyl ester, diphenyl sulphide, dithiane, thioxane, thiophene, benzothiazole, dimethyl sulphoxide, methyl ethyl sulphoxide and diethyl sulphoxide.

[0031] The addition of the organic sulphur compound can be carried out together with the catalyst, before the addition or after the addition of the catalyst. If the catalyst is reused repeatedly, the organic sulphur compound in general only needs to be added to the catalyst or to the reaction mixture on the first use. A subsequent addition of the organic sulphur compound is possible, but generally only necessary if fresh catalyst is added in place of somewhat consumed or exhausted catalyst.

Process Details

[0032] The process can be carried out either batchwise or continuously.

[0033] The process may furthermore be applied using either pure \( α,β \)-unsaturated
ketones or crude α,β-unsaturated ketones, for example from the aldol condensation, in which such α,β-unsaturated ketones can be obtained from an aldehyde and a methyl ketone.

[0034] The α,β-unsaturated ketones and the reaction medium can be added in amounts such that the wt% of the α,β-unsaturated ketones based on the total weight of the α,β-unsaturated ketones and the reaction medium is at least about 60 wt%.

[0035] The organic amine can be added in an amount from about 0.001 to about 0.025 parts by weight, e.g., about 0.002 to about 0.01 parts by weight, per part by total weight of the α,β-unsaturated ketones and the organic amine.

[0036] The Ni-containing catalyst can be added in an amount from about 0.001 to about 0.1 parts by weight, e.g., about 0.003 to about 0.04 parts by weight, per part by total weight of the α,β-unsaturated ketones and the Ni-containing catalyst, e.g., such that the weight percent of the Ni-containing catalyst based on the total weight of the Ni-containing catalyst and the α,β-unsaturated ketones to be hydrogenated is less than about 4 wt%.

[0037] The organic sulphur compound can be used in an amount from about 0.0002 to about 0.1 parts by weight, for example about 0.0004 to about 0.075, or about 0.01 to about 0.05 parts by weight, per part by total weight of the α,β-unsaturated ketones and the organic sulphur compound. For example, the organic sulphur compound can be used in amounts such that the wt% of the organic sulphur compound based on the total weight of the organic sulphur compound and the α,β-unsaturated ketones to be hydrogenated is less than about 0.50 wt%, or such that the wt% of the organic sulphur compound based on the total weight of the organic sulphur compound and the α,β-unsaturated ketones is from about 0.04 wt% to about 0.50 wt%.

[0038] In general, the process can be carried out such that the unsaturated alkyl ketone, the reaction medium, the organic amine, the Ni-containing catalyst, and the organic sulphur compound are added to the hydrogenator. The hydrogenation can be carried out at about 30°C to about 250°C, for example at about 50°C to about 140°C, and at an H₂ pressure of about 150 psi to about 1000 psi, for example about 400 psi to about 800 psi. The exothermic hydrogenation reaction can proceed for about 3 hours at about 100°C to greater than 99% conversion of the unsaturated alkyl ketone to saturated alkyl ketone in produced crude product, which also comprises trace amounts of amine hydrochloride. The crude product comprising saturated alkyl ketone can be
filtered to remove Ni-containing catalyst; filtering methods and aids known to those skilled in the art can be used, e.g., filter/body aids can be used. After the Ni-containing catalyst is filtered, a basic substance at a pH of about 8 to about 14, such as sodium hydroxide, potassium hydroxide, calcium hydroxide (for example in the form of slaked lime), calcium oxide, potassium carbonate, sodium carbonate, sodium acetate, or mixtures thereof, can be added to the crude product to convert the amine hydrochloride to a chloride, e.g., inorganic chloride, metal chloride (such as sodium chloride), or the like, and an amine, e.g., triethylamine. Then alcohol and/or water can be distilled out using means known to those skilled in the art. Substantially all of the alcohol can be distilled due to the volatility difference between the alcohol and the saturated alkyl ketone product. A benefit is that the saturated alkyl ketone product can be distilled without the need for an aqueous wash to remove salts. The saturated alkyl ketone can then be distilled, using one or more distillation columns, e.g., two distillation columns. Continuous distillation can be used.

[0039] A process according to this invention can comprise preparing a composition consisting essentially of (i) the α,β-unsaturated ketones and a reaction medium comprising alcohol or water in amounts such that the wt% of the α,β-unsaturated ketones based on the total weight of the α,β-unsaturated ketones and the reaction medium is at least about 60 wt%. (ii) organic amine, (iii) Ni-containing catalyst and (iv) organic sulphur compound R^3=S(=O)n-R^4 in which: R^3 and R^4 independently of one another denote straight-chain or branched C_1-C_12-alkyl, hydroxy-C_2-C_12-alkyl, carboxy-C_1-C_12-alkyl or phenyl, and furthermore; R^3 and R^4 may together represent -(CH=CH)(CH=CH)-, -(CH_2)_n=, -(CH_2)_{n-1}-, -(CH_2)_2-S-(CH_2)_2- or -(CH_2)_2-O-(CH_2)_2-. R^4 may additionally denote hydrogen or CO-C_1-C_12-alkyl and n assumes the value 0 or 1.

[0040] A process according to this invention can comprise preparing a composition consisting essentially of (i) the α,β-unsaturated ketones and a reaction medium comprising alcohol or water, (ii) organic amine, (iii) Ni-containing catalyst and (iv) organic sulphur compound R^3=S(=O)n-R^4 in which: R^3 and R^4 independently of one another denote straight-chain or branched C_1-C_12-alkyl, hydroxy-C_2-C_12-alkyl, carboxy-C_1-C_12-alkyl or phenyl, and furthermore; R^3 and R^4 may together represent -(CH=CH)(CH=CH)-, -(CH_2)_n=, -(CH_2)_{n-1}-, -(CH_2)_2-S-(CH_2)_2- or -(CH_2)_2-O-(CH_2)_2-. R^4 may additionally denote hydrogen or CO-C_1-C_12-alkyl and n assumes the value 0 or 1, in amounts such that the wt% of the organic sulphur compound based on the total
weight of the organic sulphur compound and the \(\alpha,\beta\)-unsaturated ketones is less than about 0.50 wt%.

[0041] A process according to this invention can comprise preparing a composition consisting essentially of (i) the \(\alpha,\beta\)-unsaturated ketones and a reaction medium comprising alcohol or water, (ii) organic amine, (iii) Ni-containing catalyst and (iv) organic sulphur compound \(R^3-S(=O)_n-R^4\) in which: \(R^3\) and \(R^4\) independently of one another denote straight-chain or branched \(C_1-C_{12}\)-alkyl, hydroxy-\(C_2-C_{12}\)-alkyl, carboxy-\(C_1-C_{12}\)-alkyl or phenyl, and furthermore; \(R^3\) and \(R^4\) may together represent \(-CH=CH=CH=CH-\), \(-(CH_2)_4-\), \(-(CH_2)_3-\), \(-(CH_2)_2S-(CH_2)_{2-}\) or \(-(CH_2)_{2-}O-(CH_2)_{2-}\), 
\(R^4\) may additionally denote hydrogen or CO-\(C_1-C_{12}\)-alkyl and \(n\) assumes the value 0 or 1, in amounts such that the weight percent of the Ni-containing catalyst based on the total weight of the Ni-containing catalyst and the \(\alpha,\beta\)-unsaturated ketones is less than about 4 wt%.

[0042] A process according to this invention can comprise combining at least the \(\alpha,\beta\)-unsaturated ketones and a reaction medium comprising alcohol or water, and the hydrogenation is carried out in the presence of at least (i) an organic amine, (ii) a Ni-containing catalyst and (iii) an organic sulphur compound \(R^3-S(=O)_n-R^4\) in which: \(R^3\) and \(R^4\) independently of one another denote straight-chain or branched \(C_1-C_{12}\)-alkyl, hydroxy-\(C_2-C_{12}\)-alkyl, carboxy-\(C_1-C_{12}\)-alkyl or phenyl, and furthermore; \(R^3\) and \(R^4\) may together represent \(-CH=CH=CH=CH-\), \(-(CH_2)_4-\), \(-(CH_2)_3-\), \(-(CH_2)_2S-(CH_2)_{2-}\) or \(-(CH_2)_{2-}O-(CH_2)_{2-}\), \(R^4\) may additionally denote hydrogen or CO-\(C_1-C_{12}\)-alkyl and \(n\) assumes the value 0 or 1, in amounts such that the wt\% of the organic sulphur compound based on the total weight of the organic sulphur compound and the \(\alpha,\beta\)-unsaturated ketones is less than about 0.50 wt% and the weight percent of the Ni-containing catalyst based on the total weight of the Ni-containing catalyst and the \(\alpha,\beta\)-unsaturated ketones is less than about 4 wt%.

[0043] A process according to this invention can comprise preparing a composition consisting essentially of (i) the \(\alpha,\beta\)-unsaturated ketones and a reaction medium comprising alcohol or water, (ii) organic amine, (iii) Ni-containing catalyst and (iv) organic sulphur compound \(R^3-S(=O)_n-R^4\) in which: \(R^3\) and \(R^4\) independently of one another denote straight-chain or branched \(C_1-C_{12}\)-alkyl, hydroxy-\(C_2-C_{12}\)-alkyl, carboxy-\(C_1-C_{12}\)-alkyl or phenyl, and furthermore; \(R^3\) and \(R^4\) may together represent \(-CH=CH=CH=CH-\), \(-(CH_2)_4-\), \(-(CH_2)_3-\), \(-(CH_2)_2S-(CH_2)_{2-}\) or \(-(CH_2)_{2-}O-(CH_2)_{2-}\),
R^4 may additionally denote hydrogen or CO–C_{1–12}–alkyl and n assumes the value 0 or 1, in amounts such that the wt% of the organic sulphur compound based on the total weight of the organic sulphur compound and the \( \alpha,\beta \)-unsaturated ketones is less than about 0.50 wt% and the weight percent of the Ni-containing catalyst based on the total weight of the Ni-containing catalyst and the \( \alpha,\beta \)-unsaturated ketones is less than about 4 wt%.

**EXAMPLES**

[0044] **Example 1**: 1-(4-chlorophenyl)-4,4-dimethylpent-1-en-3-one (794 g), methanol (360 g), 2,2'-thiodiethanol (4.8 g), Raney nickel (27 g), and triethylamine (6 g) were added to a 1-L autoclave. After purging with nitrogen and hydrogen, the autoclave was pressured to 400 psig H2 and heated to 100°C, with agitation at 1700 RPM. After reaching 100°C, the autoclave was pressured to 700 psig and periodically repressed to maintain 700 psig H2. After 2 hours (99.5% conversion), the reaction was cooled to 25°C, depressurized, and purged with nitrogen, after which the Raney nickel was filtered off. The methanol was stripped off on a rotovap, and the neat product was extracted with 2 g 85% \( \text{H}_2\text{PO}_4 \) diluted in 200 mL of water. The residual water was stripped out under vacuum, and the reaction mixture refiltered to remove traces of inorganic solids. Purification was by distillation. In this example, the weight percent of the Ni-containing catalyst based on the total weight percent of the Ni-containing catalyst and the ketones to be hydrogenated is about 3.3 wt%.

[0045] **Example 2**: 1-(4-chlorophenyl)-4,4-dimethylpent-1-en-3-one (500 g), methanol (81 g), 2,2'-thiodiethanol (0.21 g), Raney nickel 2800 (3.0 g), and triethylamine (1.85 g) were added to a 1-L autoclave in a purgebox. After purging with nitrogen and hydrogen, the autoclave was pressured to 300 psig H2 and heated to 100°C, with 1800 RPM agitation. After reaching 100°C, the pressure was increased to 500 psig and periodically repressed to maintain 500 psig H2. After 1 hour, there was a 95.7% conversion, and after 2 hours, the conversion was 99.5%, at which point the reaction was cooled to 25°C and depressurized. After purging with nitrogen, the Raney nickel was filtered off, and 0.90 g of 25% NaOH was added to the filtrate and stirred overnight. The methanol was distilled out using a 10-stage Oldershaw column, but most of the water remained in the pot. The water was distilled out by adding 24 g of toluene and azeotroping out the water and toluene with a flash distillation. The pot
residue was added to a 1-L bomb and pressure-filtered (300-400 psig nitrogen) through a 2-micron filter. The filtered product was then distilled through a 10-stage Oldershaw at 20-12 mm and a 180-190°C pot, affording a main cut (592 g) with 99.3% purity. The pot (201 g) was filtered through a 2-micron filter. In this example, the weight percent of the Ni-containing catalyst based on the total weight percent of the Ni-containing catalyst and the ketones to be hydrogenated is about 0.60 wt%; and the weight percent of the organic sulphur compound based on the total weight percent of the organic sulphur compound and the ketones to be hydrogenated is about 0.04 wt%.

[0046] Example 3: 1-(4-chlorophenyl)-4,4-dimethylpent-1-en-3-one (265 g), water (50 g), 2,2'-thiodiethanol (1.6 g), Raney nickel 2800 (10 g), and triethylamine (2.5 g) were added to a 1-L autoclave in a purgebox. After purging with nitrogen and hydrogen, the autoclave was pressurized to 400 psig H₂ and heated to 100°C, with 1850 RPM agitation. After reaching 100°C, the pressure was increased to 700 psig and periodically repressurized to maintain 700 psig H₂. After 2 hours, there was a 92.8% conversion, and the temperature was increased to 130°C. After 1 hour at 130°C, there was a 99.4% conversion, and the reaction was cooled to 25°C and depressurized. After purging with nitrogen, the Raney nickel was filtered off, and the autoclave and solids were washed with water (90 mL). In this example, the weight percent of the Ni-containing catalyst based on the total weight percent of the Ni-containing catalyst and the ketones to be hydrogenated is about 3.6 wt%.

[0047] Example 4: 1-(4-chlorophenyl)-4,4-dimethylpent-1-en-3-one (500 g), IPA (isopropanol) (81 g), 2,2'-thiodiethanol (0.22 g), Raney nickel 2800 (about 2.5 g), and tripropylamine (2.62 g) were added to a 1-L autoclave in a purgebox. After purging with three times with nitrogen (50 psig) and three times with hydrogen (200 psig), the autoclave was pressurized to 250 psig hydrogen and heated to 100°C, with 1200 RPM agitation. After reaching 100°C, the pressure was increased to 500 psig and periodically repressurized to maintain 500 psig hydrogen. After 1 hour, there was a 77% conversion, and after 2 hours, there was a 96% conversion. After 3 hours (99.1% conversion), the reaction was cooled to 25°C and depressurized. After purging three times with nitrogen (200 psig), the Raney nickel was filtered away using a Celite precoat, followed by an IPA wash (15 mL). 25% NaOH (1.3 g) was added, and the mixture was stirred for 1 hour. The IPA was distilled out (77 g distillate) by heating the pot to 200°C and holding at 200°C for 1 hour. The crude product was cooled to 25°C, filtered through a 2-micron metal filter, affording 490 g of crude product.
Example 5: 1-(4-chlorophenyl)-4,4-dimethylpent-1-en-3-one (500 g), 87:13 IPA (isopropanol):water (77 g), 2,2'-thiodiethanol (0.21 g), Raney nickel 2800 (about 2.5 g), and tripropylamine (2.64 g) were added to a 1-L autoclave in a purgebox. After purging three times with nitrogen (50 psig) and three times with hydrogen (200 psig), the autoclave was pressured to 250 psig H₂ and heated to 100°C, with 1200 RPM agitation. After reaching 100°C, the pressure was increased to 500 psig and periodically repressured to maintain 500 psig H₂. After 1 hour, there was an 81% conversion, and after 2 hours, there was a 95% conversion. After 3 hours (99.9% conversion), the reaction was cooled to 25°C and depressured. After purging three times with nitrogen (200 psig), the Raney nickel was filtered away using a Celite precoat, followed by an IPA wash (50 mL).

It is to be understood that the reactants and components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to being combined with or coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a reaction medium/solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical reaction or in forming a mixture to be used in conducting a desired reaction. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, combined, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. Whatever transformations, if any, which occur in situ as a reaction is conducted is what the claim is intended to cover. Thus the fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, combining, blending or mixing operations, if conducted in accordance with this disclosure and with the application of common sense and the ordinary skill of a chemist, is thus wholly immaterial for an
accurate understanding and appreciation of the true meaning and substance of this
disclosure and the claims thereof.

[0050] While the present invention has been described in terms of one or more
preferred embodiments, it is to be understood that other modifications may be made
without departing from the scope of the invention, which is set forth in the claims below.
CLAIMS

We Claim:

1. A process for the catalytic hydrogenation of $\alpha,\beta$-unsaturated ketones

\[ R^1\text{CH}=\text{CH}-\text{CO}-R^2 \]

in which:

- $R^1$ and $R^2$ independently of one another represent straight-chain or branched
  - $C_1$-$C_{12}$-alkyl or $C_2$-$C_{12}$-hydroxyalkyl, straight-chain or branched
  - $C_2$-$C_{12}$-alkenyl, $C_3$-$C_8$-cycloalkyl, $C_3$-$C_6$-cycloalkenyl, $C_7$-$C_{14}$-aralkyl or
  - $C_6$-$C_{12}$-aryl, where at least one of $R^1$ and $R^2$ is monosubstituted to trisubstituted
  by halogen,

to give saturated ketones $R^{11}\text{CH}_{2}$-$\text{CH}_{2}$-$\text{CO}-R^{12}$ in which:

- $R^{11}$ and $R^{12}$ assume the meaning of $R^1$ and $R^2$, respectively, with the exception
  that alkenyl and cycloalkenyl are hydrogenated to the respective alkyl or
  cycloalkyl,

wherein the process comprises combining at least the $\alpha,\beta$-unsaturated ketones and a
reaction medium comprising water or alcohol in amounts such that the wt% of the
$\alpha,\beta$-unsaturated ketones based on the total weight of the $\alpha,\beta$-unsaturated ketones and
the reaction medium is at least about 60 wt%, and the hydrogenation is carried out in
the presence of at least (i) an organic amine, (ii) a Ni-containing catalyst and (iii) an
organic sulphur compound $R^3$-$\text{S}(=\text{O})_n$-$R^4$ in which:

- $R^3$ and $R^4$ independently of one another denote straight-chain or branched
  - $C_1$-$C_{12}$-alkyl, hydroxy-$C_2$-$C_{12}$-alkyl, carboxy-$C_1$-$C_{12}$-alkyl or phenyl, and
  furthermore; $R^3$ and $R^4$ may together represent $-\text{CH}=$-$\text{CH}=$-$\text{CH}=$-$\text{CH}$-, $-(\text{CH}_2)_n$-
  $-\text{CH}_2=$-$\text{S}$-$-(\text{CH}_2)_n$- or $-(\text{CH}_2)_n$-$\text{O}$-$-(\text{CH}_2)_n$-, $R^4$ may additionally denote
  hydrogen or CO-$C_1$-$C_{12}$-alkyl and $n$ assumes the value 0 or 1.

2. The process of Claim 1 wherein the reaction medium comprises methanol,
ethanol, propanol, isopropanol, butanol, or sec butanol.

3. The process of Claim 1 wherein the organic amine comprises one or more
aliphatic or heterocyclic amines.
4. The process of Claim 1 wherein the organic amine comprises triethylamine or tripropylamine.

5. A process for the catalytic hydrogenation of $\alpha,\beta$-unsaturated ketones $R^1-\mathrm{CH}=\mathrm{CH}-\mathrm{CO}-R^2$ in which:
   - $R^1$ and $R^2$ independently of one another represent straight-chain or branched $C_1-C_{12}$-alkyl or $C_2-C_{12}$-hydroxyalkyl, straight-chain or branched $C_2-C_{12}$-alkenyl, $C_3-C_8$-cycloalkyl, $C_3-C_8$-cycloalkenyl, $C_7-C_{14}$-aralkyl or $C_8-C_{12}$-aryl, where at least one of $R^1$ and $R^2$ is monosubstituted to trisubstituted by halogen,

to give saturated ketones $R^{11}-\mathrm{CH}_2-\mathrm{CH}_2-\mathrm{CO}-R^{12}$ in which:
   - $R^{11}$ and $R^{12}$ assume the meaning of $R^1$ and $R^2$, respectively, with the exception that alkenyl and cycloalkenyl are hydrogenated to the respective alkyl or cycloalkyl,

wherein the process comprises combining at least the $\alpha,\beta$-unsaturated ketones and a reaction medium comprising water or alcohol, and the hydrogenation is carried out in the presence of at least (i) an organic amine, (ii) a Ni-containing catalyst and (iii) an organic sulphur compound $R^3-S(=O)_n-R^4$ in which:
   - $R^3$ and $R^4$ independently of one another denote straight-chain or branched $C_1-C_{12}$-alkyl, hydroxy-$C_2-C_{12}$-alkyl, carboxy-$C_1-C_{12}$-alkyl or phenyl, and furthermore; $R^3$ and $R^4$ may together represent $-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}-$, $-(\mathrm{CH}_2)_{4}-$, $-\mathrm{CH}_2-\mathrm{S}-(\mathrm{CH}_2)_2-$ or $-(\mathrm{CH}_2)_2-\mathrm{O}-(\mathrm{CH}_2)_2-$, $R^4$ may additionally denote hydrogen or CO-$C_1-C_{12}$-alkyl and $n$ assumes the value 0 or 1,

in amounts such that the wt% of the organic sulphur compound based on the total weight of the organic sulphur compound and the $\alpha,\beta$-unsaturated ketones is less than about 0.50 wt%.

6. The process of Claim 5 wherein wt% of the organic sulphur compound based on the total weight of the organic sulphur compound and the $\alpha,\beta$-unsaturated ketones is from about 0.04 wt% to about 0.50 wt%.

7. The process of Claim 5 wherein the wt% of the $\alpha,\beta$-unsaturated ketones based on the total weight of the $\alpha,\beta$-unsaturated ketones and the reaction medium is at least about 60 wt%.
8. A process for the catalytic hydrogenation of $\alpha,\beta$-unsaturated ketones $R^1$-CH=CH-CO-R$^2$ in which:

- $R^1$ and $R^2$ independently of one another represent straight-chain or branched
  - $C_1$-$C_{12}$-alkyl or $C_2$-$C_{12}$-hydroxyalkyl, straight-chain or branched
  - $C_2$-$C_{12}$-alkenyl, $C_3$-$C_8$-cycloalkyl, $C_3$-$C_8$-cycloalkenyl, $C_7$-$C_{14}$-aralkyl or
  - $C_6$-$C_{12}$-aryl, where at least one of $R^1$ and $R^2$ is monosubstituted to trisubstituted
  by halogen,

to give saturated ketones $R^{11}$-CH$_2$-CH$_2$-CO-$R^{12}$ in which:

- $R^{11}$ and $R^{12}$ assume the meaning of $R^1$ and $R^2$, respectively, with the exception
  that alkenyl and cycloalkenyl are hydrogenated to the respective alkyl or
  cycloalkyl,

wherein the process comprises combining at least the $\alpha,\beta$-unsaturated ketones and a
reaction medium comprising water or alcohol, and the hydrogenation is carried out in
the presence of at least (i) an organic amine, (ii) a Ni-containing catalyst and (iii) an
organic sulphur compound $R^3$-$S(=O)_n$-$R^4$ in which:

- $R^3$ and $R^4$ independently of one another denote straight-chain or branched
  - $C_1$-$C_{12}$-alkyl, hydroxy-$C_2$-$C_{12}$-alkyl, carboxy-$C_1$-$C_{12}$-alkyl or phenyl, and
  furthermore; $R^3$ and $R^4$ may together represent $-CH=CH-CH=CH-$, $-(CH_2)_4-$,
  $-(CH_2)_5-$, $-(CH_2)_x$-$S-(CH_2)_y$ or $-(CH_2)_x$-$O-(CH_2)_y$, $R^4$ may additionally denote
  hydrogen or CO-$C_1$-$C_{12}$-alkyl and $n$ assumes the value 0 or 1,

in amounts such that the weight percent of the Ni-containing catalyst based on the total
weight of the Ni-containing catalyst and the $\alpha,\beta$-unsaturated ketones is less than about
4 wt%.

9. The process of Claim 8 wherein the wt% of the $\alpha,\beta$-unsaturated ketones based
on the total weight of the $\alpha,\beta$-unsaturated ketones and the reaction medium is at least
about 60 wt%.

10. A process for the catalytic hydrogenation of $\alpha,\beta$-unsaturated ketones $R^1$-CH=CH-CO-R$^2$ in which:

- $R^1$ and $R^2$ independently of one another represent straight-chain or branched
  - $C_1$-$C_{12}$-alkyl or $C_2$-$C_{12}$-hydroxyalkyl, straight-chain or branched
  - $C_2$-$C_{12}$-alkenyl, $C_3$-$C_8$-cycloalkyl, $C_3$-$C_8$-cycloalkenyl, $C_7$-$C_{14}$-aralkyl or
C₆₋C₁₂₋aryl, where at least one of the radicals R¹ and R² is monosubstituted to trisubstituted by halogen,

to give saturated ketones R¹⁻⁻CH₂⁻⁻CH₂⁻⁻CO⁻⁻R¹² in which:

R¹¹ and R¹² assume the meaning of R¹ and R², respectively, with the exception that alkenyl and cycloalkenyl are hydrogenated to the respective alkyl or cycloalkyl,

wherein the process comprises preparing a composition consisting essentially of (i) the α,β⁻unsaturated ketones and a reaction medium comprising water or alcohol in amounts such that the wt% of the α,β⁻unsaturated ketones based on the total weight of the α,β⁻unsaturated ketones and the reaction medium is at least about 60 wt%, (ii) organic amine, (iii) Ni⁻containing catalyst and (iv) organic sulphur compound R³⁻⁻S(=O)n⁻⁻R⁴ in which:

R³ and R⁴ independently of one another denote straight-chain or branched C₁⁻⁻C₁₂₋alkyl, hydroxy⁻⁻C₂⁻⁻C₁₂₋alkyl, carboxy⁻⁻C₁⁻⁻C₁₂₋alkyl or phenyl, and furthermore; R³ and R⁴ may together represent -CH⁻⁻CH⁻⁻CH⁻⁻CH⁻⁻, -(CH₂)₄⁻⁻, -(CH₂)₅⁻⁻, -(CH₂)₂⁻⁻S⁻⁻(CH₂)₂⁻⁻ or -(CH₂)₂⁻⁻O⁻⁻(CH₂)₂⁻⁻, R⁴ may additionally denote hydrogen or CO⁻⁻C₁⁻⁻C₁₂₋alkyl and n assumes the value 0 or 1.

11. A process for the catalytic hydrogenation of α,β⁻unsaturated ketones R¹⁻⁻CH⁻⁻CH⁻⁻CO⁻⁻R² in which:

R¹ and R² independently of one another represent straight-chain or branched C₁⁻⁻C₁₂₋alkyl or C₂⁻⁻C₁₂⁻⁻hydroxyalkyl, straight-chain or branched C₂⁻⁻C₁₂⁻⁻alkenyl, C₃⁻⁻C₈⁻⁻cycloalkyl, C₇⁻⁻C₁₄⁻⁻aralkyl or C₆⁻⁻C₁₂⁻⁻aryl, where at least one of the radicals R¹ and R² is monosubstituted to trisubstituted by halogen,

to give saturated ketones R¹¹⁻⁻CH₂⁻⁻CH₂⁻⁻CO⁻⁻R¹² in which:

R¹¹ and R¹² assume the meaning of R¹ and R², respectively, with the exception that alkenyl and cycloalkenyl are hydrogenated to the respective alkyl or cycloalkyl,

wherein the process comprises preparing a composition comprising (i) the α,β⁻unsaturated ketones and isopropanol in amounts such that the wt% of the α,β⁻unsaturated ketones based on the total weight of the α,β⁻unsaturated ketones and the isopropanol is at least about 60 wt%, (ii) tripropylamine, (iii) Ni⁻containing catalyst and (iv) organic sulphur compound R³⁻⁻S(=O)n⁻⁻R⁴ in which:
$R^3$ and $R^4$ independently of one another denote straight-chain or branched $C_1-C_{12}$-alkyl, hydroxy-$C_2-C_{12}$-alkyl, carboxy-$C_1-C_{12}$-alkyl or phenyl, and furthermore; $R^3$ and $R^4$ may together represent $-\text{CH=CH=CH=CH}$, $-(\text{CH}_2)_4-$, $-\text{CH}_2-$, $-(\text{CH}_2)_2-S-(\text{CH}_2)_2-$ or $-(\text{CH}_2)_2-O-(\text{CH}_2)_2-$, $R^4$ may additionally denote hydrogen or CO-$C_1-C_{12}$-alkyl and $n$ assumes the value 0 or 1.
**DOCUMENTS CONSIDERED TO BE RELEVANT**

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