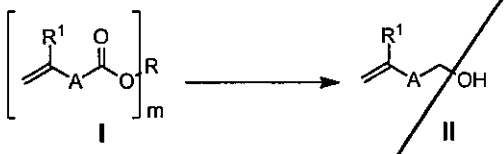
Claims:

1. A process for the chemoselective reduction of a terminally unsaturated carboxylic ester (I) to a terminally unsaturated alcohol (II) by catalytic hydrogenation, in particular, in the presence of a transition metal complex, more particularly a ruthenium (II) complex



I II

wherein A is a divalent radical containing 1 to 30 carbon atoms, which may be linear or branched, substituted or unsubstituted aliphatic, aromatic or contain both aliphatic and aromatic elements; R is a hydrocarbon radical or a radical derived from a hydrocarbon, which may be substituted or unsubstituted and saturated or unsaturated; R_1 is a hydrogen atom or a C_{1-20} linear or branched, substituted or unsubstituted alkyl or alkene group; and m is an integer from 1 to 6.

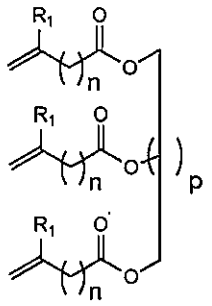
2. A process for the chemoselective reduction of a terminally unsaturated carboxylic ester to a terminally unsaturated alcohol by catalytic hydrogenation, in particular, in the presence of a transition metal complex, more particularly a ruthenium (II) complex according to claim 1



wherein R, R_1 and m are as defined in claim 1, and wherein n is an integer from 1 to 10.

3. A process according to claim 1 or claim 2, wherein the terminally unsaturated carboxylic ester is selected from the group consisting of methyl 9-decenoate, ethyl 9-decenoate, methyl 10-undecenoate or ethyl 10-undecenoate.

4. A process according to any of the preceding claims wherein the terminally unsaturated carboxylic ester (I) is represented by the formula



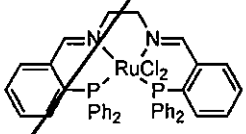
wherein p is zero or an integer from 1 to 4.

5. A process according to any of the preceding claims wherein the conversion of the terminally unsaturated carboxylic ester is greater than 80 %.

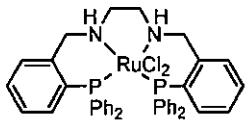
6. A process according to any of the preceding claims wherein at greater than 80 % conversion of the terminally unsaturated carboxylic ester the chemoselectivity is such that the ratio of unsaturated alcohol to saturated alcohol is 6:1 or greater, more particularly 7:1 or greater, still more particularly 8:1 or greater, still more particularly 9.1, still more particularly 10:1 or greater.

7. A process according to any of the preceding claims wherein the ruthenium complex is a complex with a tetradentate ligand wherein the coordinating groups of said tetradentate ligand consist of at least one imino or amino group and at least one phosphino group.

8. A process according to any of the preceding claims wherein the ruthenium complex is represented by the formula **4a** or **4b**



4a



4b

9. A process according to any of the preceding claims wherein the concentration of ruthenium complex is less than 0.05 mol %.

10. A process according to any of the preceding claims wherein the molar ratio of terminally unsaturated carboxylic ester/ catalyst (substrate/catalyst ratio) is greater than 2000, more particularly greater than 10000, still more particularly greater than 20000.

11. A process according to any of the preceding claims wherein the terminally unsaturated carboxylic ester is an ethyl ester or a higher ester, selected from *n*-propyl, *iso*-propyl, *n*-butyl, *tert*-butyl or *iso*-butyl ester.

12. A process according to any of the preceding claims carried out in a solvent, employed at a level of less than 100 % weight/weight (w/w) equivalents based on the amount of terminally unsaturated carboxylic ester, more particularly less than 50% w/w, still more particularly less than 25% w/w, more particularly still less than 10% w/w.

13. A process according to any of the preceding claims that is carried out in the absence of solvent.

14. A process according to any of the preceding claims carried out in a basic medium.

15. A process according to claim 14 wherein the base is a metal alkanoate, wherein the metal may be Na, K or Cs and the alkanoate is a C_1 to C_{10} alkanoate, which may be linear or branched.

16. A process according to any of the claims 14 to 15 wherein the base/solvent mixture is NaOMe/ toluene or KOMe/THF.

17. A process according to any of the preceding claims wherein a sacrificial alkene V is added to the reaction mixture



V

selected from the group consisting of terminal monosubstituted alkenes (R' = H) or 1,1-disubstituted methylene compounds (R and R' ≠ H).

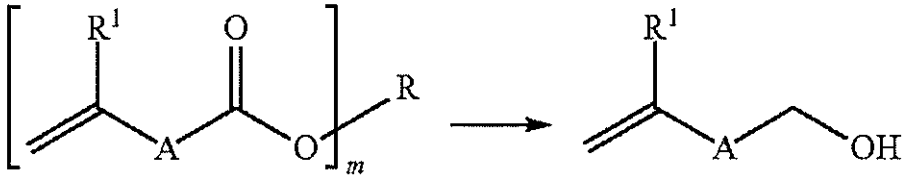
18. A process according to claim 17 in which the sacrificial alkene is added in amounts of 0.1 – 10 mol-equivalents.

19. A process according to claim 17 or 18 in which the sacrificial alkene is selected from the group of substituted styrenes including preferably styrene.

20. A method of forming 9-decenol by the chemoselective reduction of the carboxylic ester methyl 9-decenoate or ethyl 9-decenoate according to a process as defined in any of the claims 1 through 18.

Claims

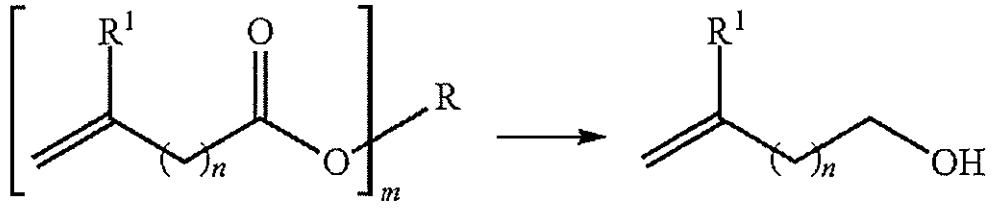
1. A process for the chemoselective reduction of a terminally unsaturated carboxylic ester (I) to a terminally unsaturated alcohol (II)



I II

wherein A is a divalent radical containing 1 to 30 carbon atoms, which may be linear or branched, substituted or unsubstituted aliphatic, aromatic or contain both aliphatic and aromatic elements; R is a hydrocarbon radical or a radical derived from a hydrocarbon, which may be substituted or unsubstituted and saturated or unsaturated; R_1 is a hydrogen atom or a $C_{1\text{-}20}$ linear or branched, substituted or unsubstituted alkyl or alkene group; and m is an integer from 1 to 6, by catalytic hydrogenation in the presence of a ruthenium (II) complex, wherein the concentration of the ruthenium (II) complex is less than 0.05 mol %.

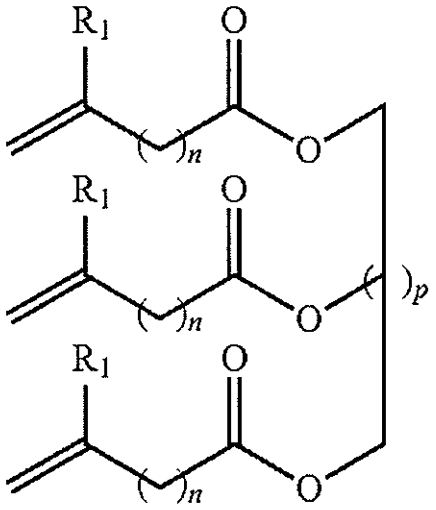
2. The process for the chemoselective reduction of a terminally unsaturated carboxylic ester to a terminally unsaturated alcohol by catalytic hydrogenation in the presence of the ruthenium (II) complex according to claim **1**



wherein R, R_1 and m are as defined, and wherein n is an integer from 1 to 10.

3. The process according to claim **1**, wherein the terminally unsaturated carboxylic ester is selected from the group consisting of methyl 9-decenoate, ethyl 9-decenoate, methyl 10-undecenoate and ethyl 10-undecenoate.

4. The process according to claim **1** wherein the terminally unsaturated carboxylic ester (I) is represented by the formula



wherein p is zero or an integer from 1 to 4.

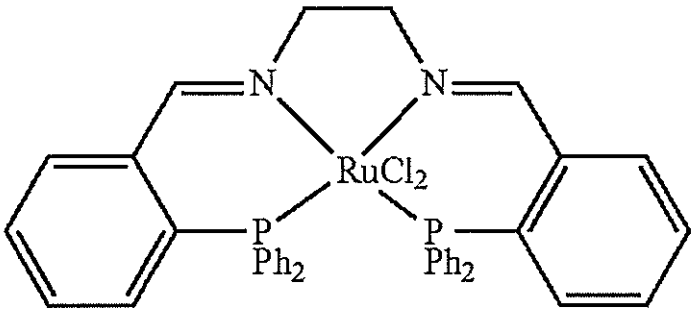
5. The process according to claim **1** wherein the conversion of the terminally unsaturated carboxylic ester is greater than 80%.

6. The process according to claim **1** wherein at greater than 80% conversion of the terminally unsaturated carboxylic ester the chemoselectivity is such that the ratio of unsaturated alcohol to saturated alcohol is 6:1 or greater, optionally 7:1 or greater, further optionally 8:1 or greater, further optionally 9:1, further optionally 10:1 or greater.

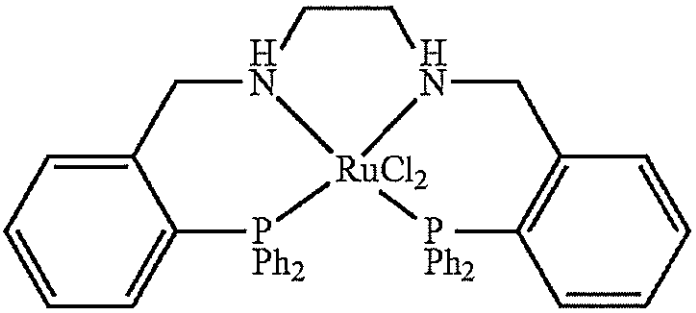
7. The process according to claim **1** wherein the ruthenium complex is a complex with a tetradentate ligand wherein the coordinating groups of said tetradentate ligand consist of at least one imino or amino group and at least one phosphino group.

8. The process according to claim **1** wherein the ruthenium complex is represented by the formula 4a or 4b

4a



4b



9. The process according to claim **1** wherein the molar ratio of terminally unsaturated carboxylic ester/ catalyst (substrate/catalyst ratio) is greater than 2000, optionally greater than 10000, further optionally greater than 20000.

10. The process according to claim **1** wherein the terminally unsaturated carboxylic ester is an ethyl ester or a higher ester, selected from n-propyl, iso-propyl, n-butyl, tert-butyl or iso-butyl ester.

11. The process according to claim **1** carried out in a solvent, employed at a level of less than 100% weight/weight (w/w) equivalents based on the amount of terminally unsaturated carboxylic ester, optionally less than 50% w/w, further optionally less than 25% w/w, further optionally less than 10% w/w.

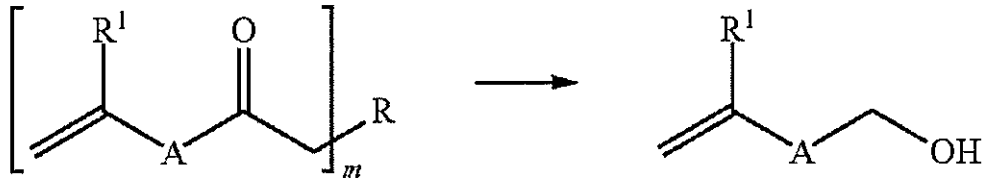
12. The process according to claim **1** that is carried out in the absence of solvent.

13. The process according to claim **1** carried out in a basic medium.

14. The process according to claim **13** wherein the base is a metal alkanoate, wherein the metal may optionally be Na, K or Cs and the alkanoate is a C_1 to C_{10} alkanoate, which may be linear or branched.

15. The process according to claim **13** wherein the base/ solvent mixture is NaOMe/ toluene or KOMe/THF.

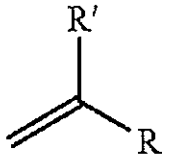
16. A process for the chemoselective reduction of a terminally unsaturated carboxylic ester (I) to a terminally unsaturated alcohol (II) by catalytic hydrogenation, optionally in the presence of a transition metal complex, further optionally in the presence of a ruthenium (II) complex



I II

wherein A is a divalent radical containing 1 to 30 carbon atoms, which may be linear or branched, substituted or unsubstituted aliphatic, aromatic or contain both aliphatic and aromatic elements; R is a hydrocarbon radical or a radical derived from a hydrocarbon, which may be substituted or unsubstituted and saturated or unsaturated; R_1 is a hydrogen atom or a C_{1-20} linear or branched, substituted or unsubstituted alkyl or alkene group; and m is an integer from 1 to 6, and wherein a sacrificial alkene V is added to the reaction mixture

V



selected from the group consisting of terminal monosubstituted alkenes wherein R'=H, and 1,1-disubstituted methylene compounds wherein R and R'≠H.

17. The process according to claim **16** in which the sacrificial alkene is added in amounts of 0.1-10 mol-equivalents.

18. The process according to claim **16** in which the sacrificial alkene is selected from the group of substituted styrenes or styrene.

19. A method of forming 9-decenol by the chemoselective reduction of the carboxylic ester methyl 9-decenoate or ethyl 9-decenoate according to the process as defined in claim **3**.

20. A method of forming 9-decenol by the chemoselective reduction of the carboxylic ester methyl 9-decenoate or ethyl 9-decenoate according to the process as defined in claim **16**.