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(54) Title: PROCESS FOR THE PRODUCTION OF 4-ALKANOYLOXY-2-METHYLBUTANOIC ACID

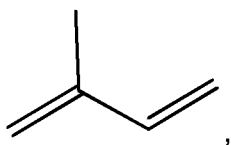
(57) Abstract: The present invention relates to an improved process for the production of 4-alkanoyloxy-2-methylbutanoic acid, as well as to the use of such compounds in organic syntheses, especially in processes forming intermediates (building blocks) for the synthesis of organic compounds comprising isoprene (isoterpene) units, such as β -carotene or other carotenoids (e.g. canthaxanthin, zeaxanthin or astaxanthin) or as vitamin E or vitamin A as well as other structurally similar compounds.



PROCESS FOR THE PRODUCTION OF 4-ALKANOYLOXY-2-METHYLBUTANOIC ACID

The present invention relates to an improved process for the production of 4-alkoxy-2-methylbutanoic acid, as well as to the use of such compounds in organic syntheses, especially in processes forming intermediates (building blocks) for the synthesis of organic compounds comprising isoprene (=isoterpene) units, such as β -carotene or other carotenoids (e.g. canthaxanthin, zeaxanthin or astaxanthin) or as vitamin E or vitamin A as well as other structurally similar compounds.

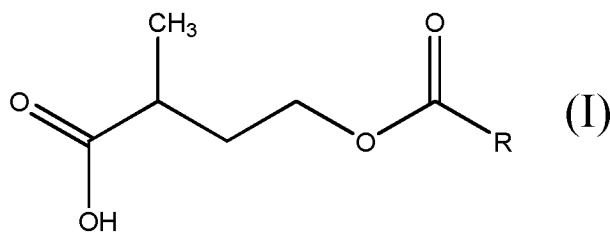
Isoprene, which has the following chemical structure



is an important chemical unit for a group of chemical compounds known as isoprenoids. Carotenoids as well as vitamin E as mentioned above are i.e. such isoprenoids.

Due to the importance of these compounds and the complexity of the synthesis thereof, there is always a need for improved processes of their production.

4-alkanoyloxy-2-methylbutanoic acid, the compound of formula (I)



wherein R signifies a C₁-C₁₅ alkyl moiety or a C₂-C₁₈ alkenyl moiety,

is an important compound (building block, starting compound) in such organic synthesis (for the production of isoprenoids).

When R is a C₁-C₁₅ alkyl moiety, then preferably the alkyl moiety is linear. Especially preferred alkyl moieties are methyl, ethyl and pentadecyl.

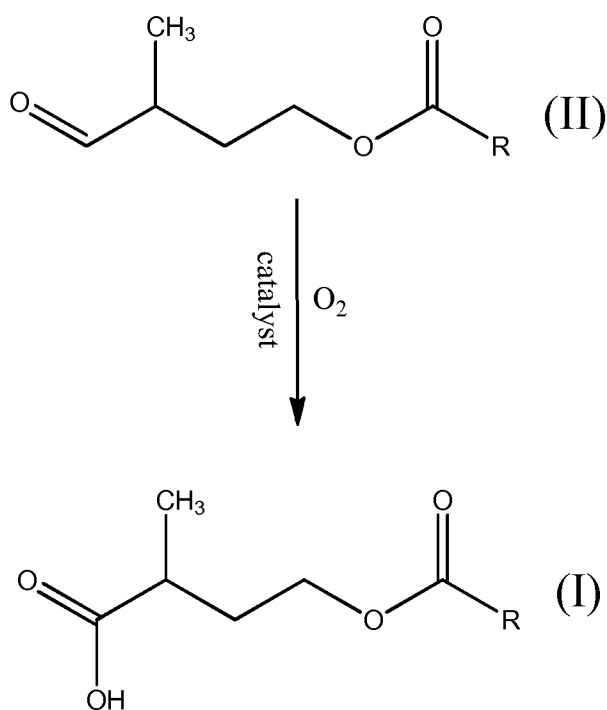
When R is a C₂-C₁₈ alkenyl moiety, there are one or more C-C double bonds. Preferably the alkenyl moiety is unbranched.

Compounds of formula (I) are known from the prior art, i.e. from Ali and Alper, J. Mol. Catal. 77 (1992), 7 – 13.

Described therein, there is also a process wherein a compound of formula (I) is obtained. But the therein disclosed and described process of production only allows to obtain compounds of formula (I) in low yield (12%) and in mixtures with other (main) products, so that the compounds of formula (I) have to be isolated.

The goal of the present invention was to provide an improved process of production of compounds of formula (I).

Surprisingly, it was found out that a compound of formula (I) can be obtained in an excellent yield by the following process

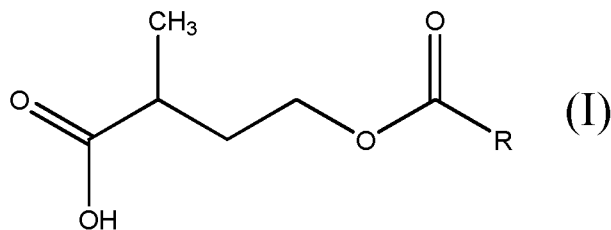


wherein

R signifies a C₁-C₁₅ alkyl moiety or a C₂-C₁₈ alkenyl moiety, and

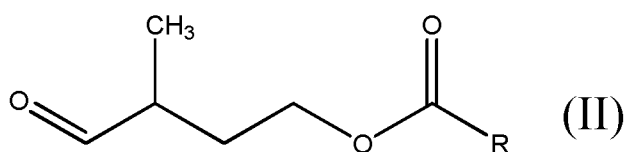
when at least one transition metal salt is used as a catalyst in the oxidation process.

- 5 Therefore the present invention relates to a process of production of a compound of formula (I)



wherein R signifies a C₁-C₁₅ alkyl moiety or a C₂-C₁₈ alkenyl moiety,

- 10 wherein a compound of formula (II)

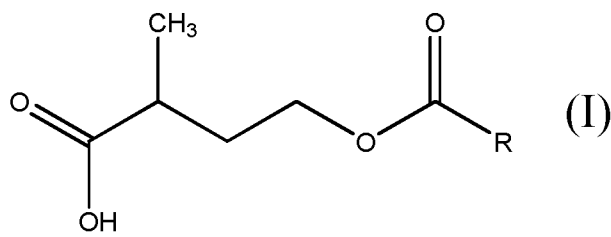


with R as defined as for compound of formula (I)

is oxidised by using an oxygen-containing gas and characterised in that

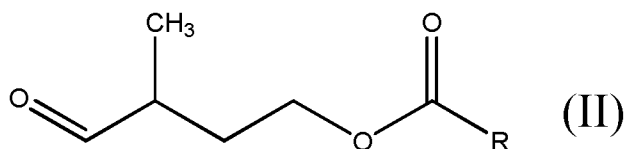
- 15 at least one transition metal salt is used as a catalyst.

Preferably, the present invention relates to a process of production of a compound of formula (I)



- 20 wherein R signifies a linear C₁-C₁₅ alkyl moiety (preferably methyl, ethyl and penta-decyl),

wherein a compound of formula (II)



with R as defined as for compound of formula (I)

is oxidised by using an oxygen-containing gas and characterised in that

5 at least one transition metal salt is used as a catalyst.

In the context of the present patent application the term “*transition metal*” is defined as any element in the d-block of the periodic table, which includes groups 3 to 12 on the periodic table. The f-block is also (in the form of the lanthanide and actinide series) part of the definition.

The transition metal is the cation of the salt and the anion can be organic as well inorganic.

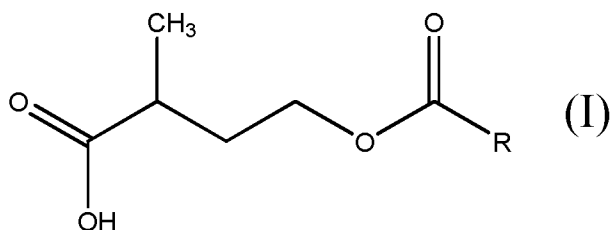
Preferred transition metals are Cu, Co, Fe and Cr.

The anion of the transition metal salt is not crucial for the invention. Any usually used anion can be the counterion. Preferred anions are halides (such as Cl⁻, Br⁻ or I⁻), PO₄³⁻, SO₄²⁻ or ⁻O(CO)CH₃).

It is possible to use a single transition metal salt as well as mixtures thereof.

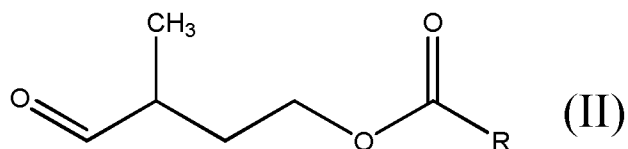
Preferred salts are Co(O(CO)CH₃)₂, Cu(O(CO)CH₃)₂, CoSO₄, CuSO₄, Fe₂(SO₄)₃, CoCl₂, CuCl₂ and FeCl₃.

Therefore the present invention relates to a preferred process of production of a compound of formula (I)



25

wherein R signifies a C₁-C₁₅ alkyl moiety or a C₂-C₁₈ alkenyl moiety, wherein a compound of formula (II)



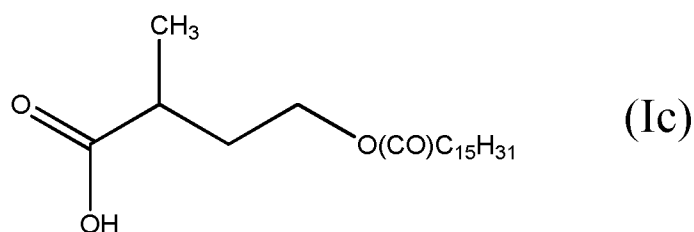
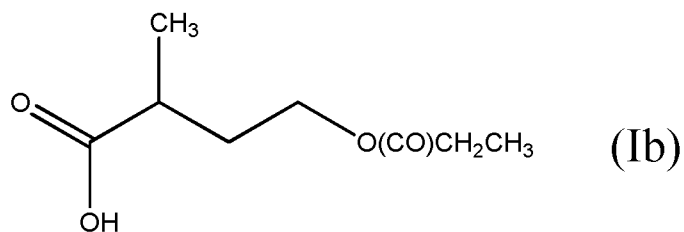
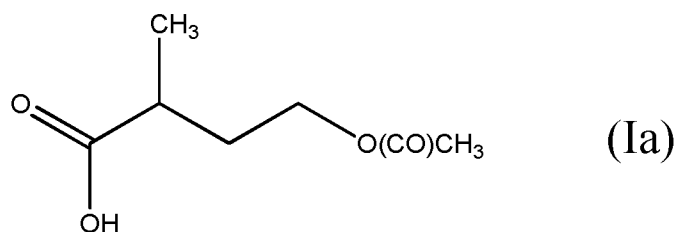
with R as defined as for compound of formula (I)

is oxidised by using an oxygen-containing gas and

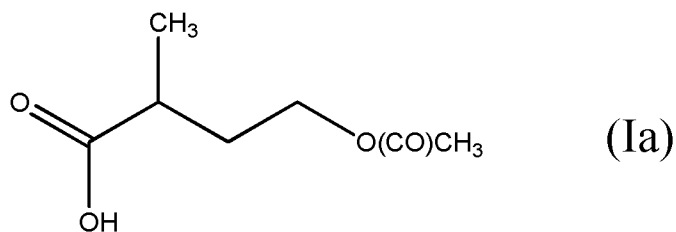
5 characterised in that

at least one transition metal salt selected from the group consisting of $\text{Co}(\text{O}(\text{CO})\text{CH}_3)_2$, $\text{Cu}(\text{O}(\text{CO})\text{CH}_3)_2$, CoSO_4 , CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoCl_2 , CuCl_2 and FeCl_3 is used as a catalyst.

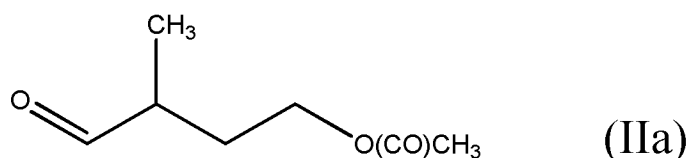
10 Preferred compounds of formula (I) are



15 Therefore the present invention relates to a preferred process of production of a compound of formula (Ia)



wherein a compound of formula (IIa)

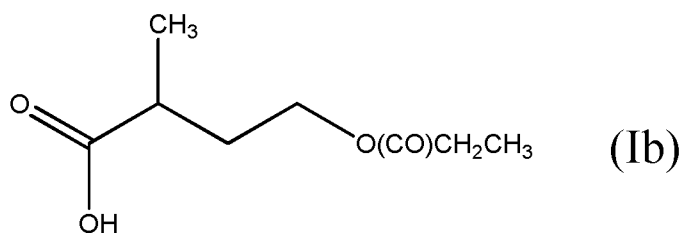


is oxidised by using an oxygen-containing gas and

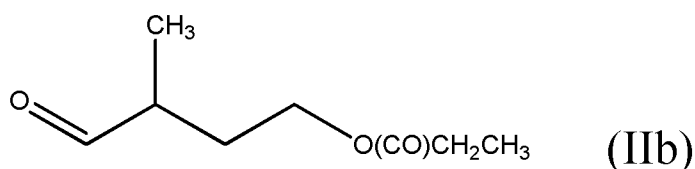
5 characterised in that

at least one transition metal salt selected from the group consisting of $\text{Co}(\text{O}(\text{CO})\text{CH}_3)_2$, $\text{Cu}(\text{O}(\text{CO})\text{CH}_3)_2$, CoSO_4 , CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoCl_2 , CuCl_2 and FeCl_3 is used as a catalyst.

10 Therefore the present invention also relates to a preferred process of production of a compound of formula (Ib)



wherein a compound of formula (IIb)



15

is oxidised by using an oxygen-containing gas and

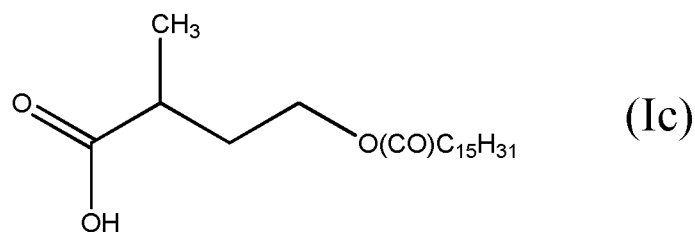
characterised in that

at least one transition metal salt selected from the group consisting of $\text{Co}(\text{O}(\text{CO})\text{CH}_3)_2$, $\text{Cu}(\text{O}(\text{CO})\text{CH}_3)_2$, CoSO_4 , CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoCl_2 , CuCl_2 and

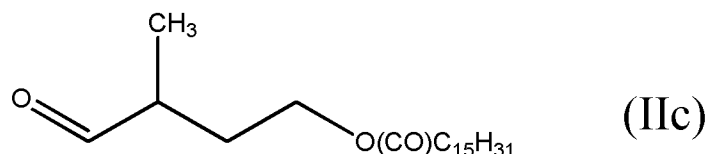
20

FeCl_3 is used as a catalyst.

Therefore the present invention also relates to a preferred process of production of a compound of formula (Ic)



wherein a compound of formula (IIc)



5 is oxidised by using an oxygen-containing gas and characterised in that

at least one transition metal salt selected from the group consisting of $\text{Co}(\text{O}(\text{CO})\text{CH}_3)_2$, $\text{Cu}(\text{O}(\text{CO})\text{CH}_3)_2$, CoSO_4 , CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoCl_2 , CuCl_2 and FeCl_3 is used as a catalyst.

10

The process of the present invention is a catalytic oxidation. The oxidant used in the process is a gas comprising O_2 . It can be pure O_2 gas as well as a mixture which comprises O_2 (such e.g. air).

Preferably the process according to the present invention is carried by using air as

15 oxidant.

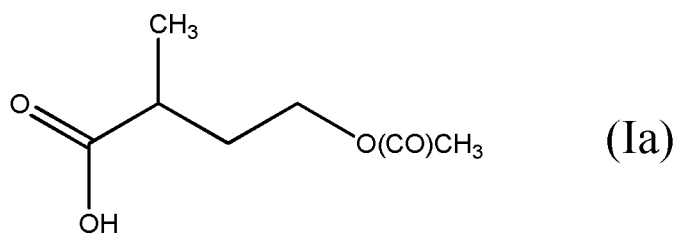
The process according to the present invention can be carried under pressure (up to 20bar) as well as at ambient pressure.

20 Preferably the process according to the present invention is carried out ambient pressure.

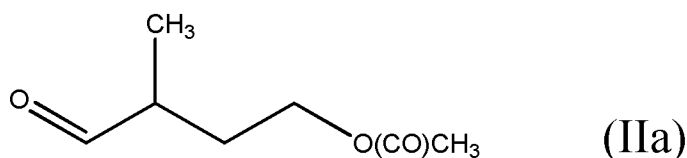
The transition metal salt catalyst (as well as a mixture of such salts) is used in catalytic amounts.

25 Usually the transition metal salt catalyst (as well as a mixture of such salts) is used in an amount of 0.0005 – 0.1 mol equivalent (related to the mol of compound of formula (II)).

Therefore the present invention relates to a preferred process of production of a compound of formula (Ia)



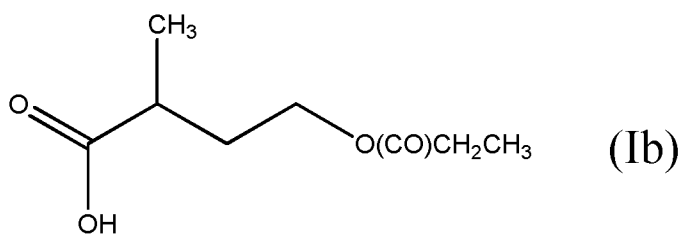
wherein a compound of formula (IIa)



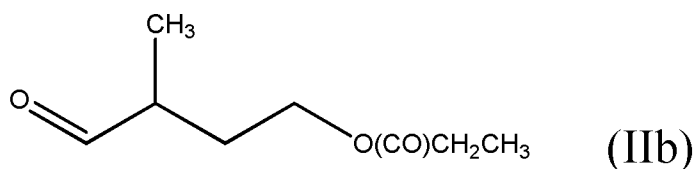
is oxidised by using an oxygen-containing gas and characterised in that

0.0005 – 0.1 mol equivalent (related to the mol of compound of formula (IIa)) of at least one transition metal salt selected from the group consisting of $\text{Co}(\text{O}(\text{CO})\text{CH}_3)_2$, $\text{Cu}(\text{O}(\text{CO})\text{CH}_3)_2$, CoSO_4 , CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoCl_2 , CuCl_2 and FeCl_3 is used as a catalyst.

Therefore the present invention also relates to a preferred process of production of a compound of formula (Ib)



wherein a compound of formula (IIb)

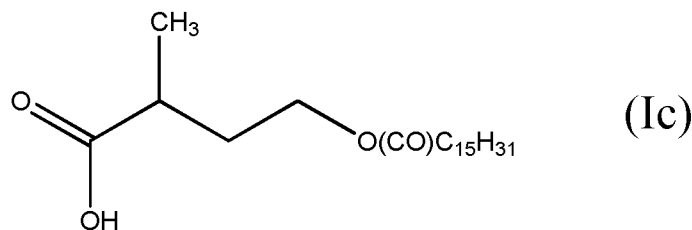


is oxidised by using an oxygen-containing gas and characterised in that

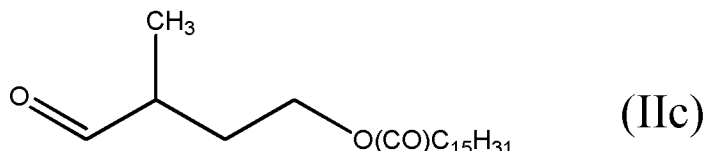
0.0005 – 0.1 mol equivalent (related to the mol of compound of formula (IIb)) of at least one transition metal salt selected from the group consisting of $\text{Co}(\text{O}(\text{CO})\text{CH}_3)_2$,

$\text{Cu}(\text{O}(\text{CO})\text{CH}_3)_2$, CoSO_4 , CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoCl_2 , CuCl_2 and FeCl_3 is used as a catalyst.

Therefore the present invention also relates to a preferred process of production of
 5 a compound of formula (Ic)



wherein a compound of formula (IIc)



10 is oxidised by using an oxygen-containing gas and characterised in that

0.0005 – 0.1 mol equivalent (related to the mol of compound of formula (IIc)) of at least one transition metal salt selected from the group consisting of $\text{Co}(\text{O}(\text{CO})\text{CH}_3)_2$, $\text{Cu}(\text{O}(\text{CO})\text{CH}_3)_2$, CoSO_4 , CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoCl_2 , CuCl_2 and FeCl_3 is used as a
 15 catalyst.

The process according to present invention is usually carried out at temperatures of -10°C – 150°C , preferably 0°C – 80°C , more preferably 15°C – 70°C .

20 The process according to the present invention is usually carried out in a polar aprotic or polar protic solvent, as well as in mixtures of such solvents. Suitable solvents are esters (such as ethyl acetate), carbonates (such as ethylene carbonate), carboxylic acids (such as acetic acid, formic acid), alcohols (such methanol, ethanol, propanol, isopropanol), DMSO, DMF, acetone, dichloroethane, dichloromethane
 25 and chloroform.

It is also possible that the process is carried out without any solvent.

The product of the process according to the present invention (compound of formula (I)) can be used in organic synthesis.

Usually the compound of formula (I) is used in the synthesis of an intermediate, which is then used for the synthesis of vitamin E, vitamin A or β -carotene, can-
5 thaxanthin, zeaxanthin or astaxanthin. Such process are known from the prior art.

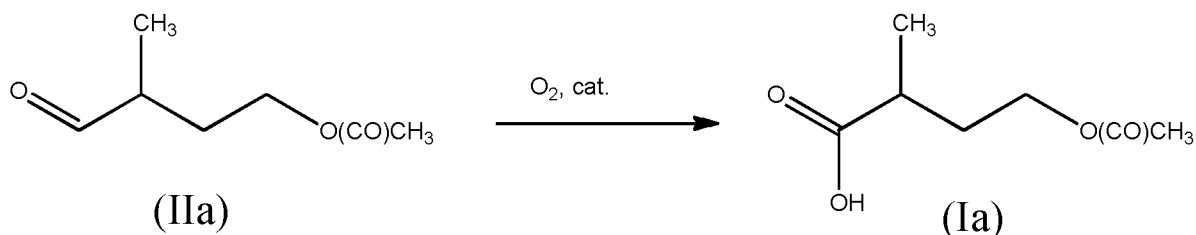
The present examples serve to illustrate the present invention.

All parts given in the examples are related to weight and the temperatures are given in °C, if not otherwise stated.

Examples

Example 1

5



500 mg (3.34 mmol) of compound of formula (IIa) were dissolved in 10 ml of ethyl acetate (from Fluka).

- 10 8.0 mg (0.03 mmol = 0.01 mol eq) of the catalyst $\text{Cu}(\text{OAc})_2 \times 4 \text{H}_2\text{O}$ (from Fluka) were added. The reaction mixture was heated to 40 °C and air was bubbled through the solution for 20 h. The reaction mixture was washed with water (2 x 15 ml) and the combined aqueous phases were extracted with ethyl acetate (2 x 25 ml). The combined organic phases were dried over sodium sulfate, filtered, and concentrated
- 15 in vacuo (45 °C, 200 to 20 mbar). A liquid was obtained which comprised the compound of formula (Ia) in 87.3% yield.

Example 2

- 20 500 mg (3.34 mmol) of compound of formula (IIa) were dissolved in 10 ml of ethyl acetate (from Fluka).

- 9.0 mg (0.03 mmol = 0.01 mol eq) of the catalyst $\text{Co}(\text{SO}_4)_2 \times 5 \text{H}_2\text{O}$ (from Sigma) were added. The reaction mixture was heated to 40 °C and air was bubbled through the solution for 20 h. The reaction mixture was washed with water (1 x 20 ml, 1 x 10
- 25 ml) and saturated NaCl solution (10 ml). The combined aqueous phases were extracted with ethyl acetate (2 x 10 ml). The combined organic phases were dried over sodium sulfate, filtered, and concentrated in vacuo (45 °C, 300 to 10 mbar). The product was obtained as a liquid in 59% yield.

Example 3

500 mg (3.34 mmol) of compound of formula (IIa) were dissolved in 10 ml of ethyl acetate (from Fluka).

0.6 mg (0.003 mmol) of the catalyst $\text{CuCl}_2 \times 2 \text{H}_2\text{O}$ (from Acros) were added. The reaction mixture was heated to 40 °C and air was bubbled through the solution for 3 h. All volatiles were removed in vacuo (45 °C, 180 to 20 mbar). The product was obtained as a liquid in 83% yield.

Example 4 (Comparative Example)

500 mg (3.34 mmol) of compound of formula (IIa) were dissolved in 10 ml of ethyl acetate (from Fluka).

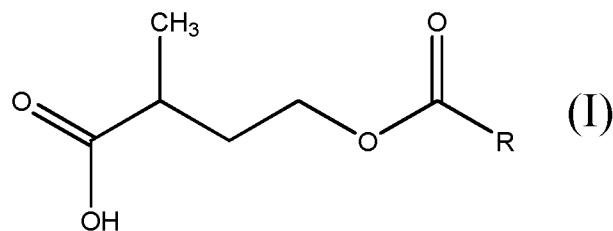
36 mg (0.03 mmol = 0.01 mol eq) of the catalyst Pd/C (10%) were added. The reaction mixture was heated to 40 °C and air was bubbled through the solution for 17 h.

All volatiles were removed in vacuo (45 °C, 180 to 20 mbar). The product was obtained as a liquid in 45% yield.

From example 4 it can be seen that another (commonly used) catalyst does not lead to the yields that were achieved with the process as described and claimed by the present patent application.

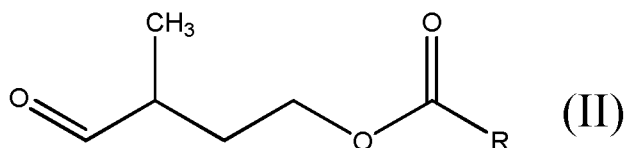
Claims

1. A process of production of a compound of formula (I)



5

wherein R signifies a C₁-C₁₅ alkyl moiety or a C₂-C₁₈ alkenyl moiety,
wherein a compound of formula (II)



with R as defined as for compound of formula (I)

- 10 is oxidised by using an oxygen-containing gas and
characterised in that
at least one transition metal salt is used as a catalyst.

2. Process according to claim 1, wherein the transition metal of the transition
15 metal salt is chosen from the group consisting of Cu, Co, Fe and Cr.

3. Process according to any of the preceding claims, wherein the anion of the
transition metal salt is chosen from the group consisting of halides (such as Cl⁻, Br⁻
or I⁻), PO₄³⁻, SO₄²⁻ or ⁻O(CO)CH₃).

20

4. Process according to any of the preceding claims, wherein the transition met-
al is chosen from the group consisting of Co(O(CO)CH₃)₂, Cu(O(CO)CH₃)₂, CoSO₄,
CuSO₄, Fe₂(SO₄)₃, CoCl₂, CuCl₂ and FeCl₃.

- 25 5. Process according to any of the preceding claims, wherein R in formula (I)
and in formula (II) is an alkyl moiety which is linear (preferably methyl, ethyl and
pentadecyl).

6. Process according to any of the preceding claims, wherein the oxygen-containing gas is O₂ gas or air.

7. Process according to any of the preceding claims, wherein the process is carried out under pressure (up to 20 bar) or at ambient pressure.

8. Process according to any of the preceding claims, wherein the transition metal salt catalyst (as well as a mixture of such salts) is used in an amount of 0.0005 – 0.1 mol equivalent (related to one mol of compound of formula (II)).

10

9. Process according to any of the preceding claims, wherein the process is carried out at temperatures of - of -10°C – 150°C, preferably 0°C – 80°C, more preferably 15°C – 70°C. C.

15 10. Process according to any of the preceding claims, wherein the process is carried out in a polar aprotic or polar protic solvent (preferably in esters (such as ethyl acetate), carbonates (such as ethylene carbonate), carboxylic acids (such as acetic acid, formic acid), alcohols (such methanol, ethanol, propanol, isopropanol), DMSO, DMF, acetone, dichloroethane, dichloromethane and/or chloroform).

20

11. Process according to anyone of claims 1 – 9, wherein the process is carried out without any solvent.

12. Use of a compound of formula (I) as defined in claim 1 in organic synthesis, especially in the process of producing isoprenoids.

25

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/061605

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C67/29 C07C69/14 C07C69/02 C07C69/52
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

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

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

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 665 091 A (HOFFMAN WILLIAM F [US]) 12 May 1987 (1987-05-12) example 2b ----- -/--	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

29 August 2013

Date of mailing of the international search report

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PCT/EP2013/061605

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>BASSAM EL ALI ET AL: "FORMIC ACID-PALLADIUM ACETATE-1,4-BIS(DIPHENYLPHOSPHINO)BUTANE: AN EFFECTIVE CATALYTIC SYSTEM FOR REGIOSELECTIVE HYDROCARBOXYLATION OF SIMPLE AND FUNCTIONALIZED OLEFINS", JOURNAL OF MOLECULAR CATALYSIS, ELSEVIER, NL, vol. 77, no. 1, 1 January 1992 (1992-01-01), pages 7-13, XP009052481, ISSN: 0304-5102, DOI: 10.1016/0304-5102(92)80179-K cited in the application table 1</p> <p style="text-align: center;">-----</p>	1-11
A	<p>OHTA T ET AL: "ASYMMETRIC HYDROGENATION OF UNSATURATED CARBOCYLIC ACIDS CATALYZED BY BINAP-RUTHENIUM(II) COMPLEXES", JOURNAL OF ORGANIC CHEMISTRY, ACS, US, vol. 52, no. 14, 10 July 1987 (1987-07-10), pages 3174-3176, XP000577195, ISSN: 0022-3263, DOI: 10.1021/J000390A043 table I</p> <p style="text-align: center;">-----</p>	1-11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/061605

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-11

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11

process of production of a compound of formula (I)

2. claim: 12

use of a compound of formula (I) in organic synthesis.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/061605

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4665091	A	12-05-1987	NONE
