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(54) Title: METHOD OF CLEAVING OLEIC ACID AND/OR DERIVATIVES THEREOF

(57) Abstract: In accordance with the present subject matter there is provided a method of cleaving oleic acid and/or derivatives thereof, the method comprising oxidatively cleaving oleic acid, and/or derivatives thereof with oxygen, hydrogen peroxide, a catalyst, a phase transfer catalyst, and a solvent in an amount from 0 to 30 wt % with respect to the oleic acid, and/or derivatives thereof.

METHOD OF CLEAVING OLEIC ACID AND/OR DERIVATIVES THEREOF

CROSS-REFERENCE TO PREVIOUS APPLICATIONS

[0001] This application claims priority to Indian provisional application No. 201621041887 filed on 7 December 2016. The whole content of this application is incorporated herein by reference for all purposes.

TECHNICAL FIELD

[0002] The present disclosure relates to a method of cleaving unsaturated fatty acids, more precisely oleic acid, and/or derivatives thereof. The present disclosure further relates to a method of producing long chain carboxylic acids.

BACKGROUND

[0003] Long chain carboxylic acids find a wide range of applications in various chemical industries, such as, pharmaceuticals, and agrochemicals. Preparation of long chain carboxylic acids is a challenging task due to high unpredictability of chemical arts. One of the most common and successful techniques for the preparation of long chain carboxylic acid is by way of oxidative cleavage of unsaturated fatty acids.

[0004] This method involves the cleavage of the double bond of unsaturated fatty acids by means of a strong oxidant resulting into two saturated fatty acid molecules. However, there are several drawbacks associated with this technique, such as low selectivity, low yield, and lower than expected level of mass transfer from one medium to another. Selectivity in cleavage is one of the major issues related to the oxidative cleavage technique as all the unsaturated portions of the fatty acids are broken down irrespective of the desired product which in turn reduces the yield of the desired product.

[0005] To rectify the aforesaid problem, the prior arts provide solution by performing the reaction in two steps, i.e., first step involves the oxidation of the double bond to form a vicinal diol and the second step involves cleavage of carbon-carbon bond between the two hydroxyl groups to obtain a carboxylic acid with reduced chain length, and/or carrying out the reaction in a higher amount of an organic solvent. Both the solutions have their inherent drawbacks. US9035079 in its background mentions the drawback of the two-step method, i.e., a two-step method is not optimum for application on an industrial scale and also the use of two different catalysts in different steps is very expensive. Further, it also describes that, "*it is restricting to carry out two separate steps, notably because it is necessary to perform a reactor transfer*".

[0006] CN104447279 discloses a method for synthesizing azelaic acid starting from oleic acid and using a combination of hydrogen peroxide and potassium permanganate. The method comprises the steps of mixing oleic acid, a phosphotungstic acid catalyst, and benzyl triethyl ammonium chloride as phase transfer catalyst, followed by introduction of oxygen and further addition of potassium permanganate, and hydrogen peroxide solution to the reaction mixture. The method described in the aforementioned document uses a combination of potassium permanganate and oxygen as oxidants in addition to hydrogen peroxide. However, the use of potassium permanganate leads to unwanted side products, such as manganese salts, etc. which in turn reduces the yield of the desired product and increases the number of purification steps. Besides, the process described in this document uses a high amount of hydrogen peroxide which renders it economically unattractive.

[0007] US5939572 teaches a method of contacting an olefinic compound or a vicinal dihydroxy compound with oxygen in the presence of a protic organic solvent, an inorganic oxide catalyst and a peroxidant such as hydrogen peroxide or a peralkanoic acid. The inorganic oxide catalyst is selected from an oxide of tungsten, molybdenum, niobium, vanadium, tantalum, titanium, or yttrium. To achieve the desired product, this prior art method uses a very high amount of protic solvent. However, there is a high risk of the formation of an explosive mixture of the organic solvent, such as alcohol, and oxygen (*Practical dihydroxylation and C-C cleavage of unsaturated fatty acid, Journal of Molecular Catalysis A: Chemical 150 (1999), 105–111).*

[0008] Therefore, there is a need to provide an economical method for cleaving unsaturated fatty acids to obtain long chain carboxylic acids by minimizing the above mentioned drawbacks.

[0009] For convenience, before further description of the present disclosure, certain terms employed in the specification, and examples are collected here. These definitions should be read in the light of the remainder of the disclosure and understood as by a person of skill in the art. The terms used herein have the meanings recognized and known to those of skill in the art, however, for convenience and completeness, particular terms and their meanings are set forth below.

[0010] The articles "a", "an" and "the" are used to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. The term "and/or" includes the meanings "and", "or" and also all the other possible combinations of the elements connected to this term.

[0011] The terms "comprise" and "comprising" are used in the inclusive, open sense, meaning that additional elements may be included. Throughout this specification, unless the context requires otherwise the word "comprise", and variations, such as "comprises" and "comprising", will be understood to imply the inclusion of a stated element or step or group of element or steps but not the exclusion of any other element or step or group of element or steps.

[0012] The term "including" is used to mean "including but not limited to". "Including" and "including but not limited to" are used interchangeably.

[0013] The term "between" should be understood as being inclusive of the limits.

[0014] The term "salts" includes a compound that results from the neutralization reaction of unsaturated fatty acid and a base. The base includes both inorganic base for example alkali metal (e.g. sodium or potassium) and alkali earth metal (e.g. calcium or magnesium) hydroxides and organic bases, for example alkyl amines, arylalkyl amines, and heterocyclic amines.

[0015] The term "ester" includes an organic compound obtained by the replacement of the hydrogen of the unsaturated fatty acid by an alkyl or other organic group for example aryl, cycloalkyl, heteroaryl which can be further substituted.

[0016] Ratios, concentrations, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a temperature range of about 60°C to about 100°C should be interpreted to include not only the explicitly recited limits of about 60°C to about 100°C, but also to include sub-ranges, such as 65°C to 95°C, 80°C to 100°C, and so forth, as well as individual amounts, including fractional amounts, within the specified ranges, such as 65.2°C, 85.6°C, and 96.3°C, for example.

[0017] In reaction media as in the present invention, the decomposition of hydrogen peroxide results in substantial enrichment of oxygen (O_2). Bubbles of oxygen bursting at the surface of the reaction medium in turn produce an electrostatic field sufficient to ignite protic solvents/flammable solvents. Each bubble bursting at the surface is oxygen rich and solvent saturated and thus is extremely sensitive to ignition. However, for a successful oxidative cleavage, prior art teaches to include both the hydrogen peroxide as oxidant and the presence of high amount of organic solvent. Thus, as a remedy to the above mentioned facts and for

the safety purpose, the present disclosure provides a safe and economical method for cleaving unsaturated fatty acids to obtain long chain carboxylic acids.

[0018] The present disclosure provides an oxidative cleavage of olefinic group to acid functionality for the synthesis of aliphatic diacids from unsaturated a fatty acid using a stoichiometric amount of hydrogen peroxide. Aliphatic diacids are widely used for making polyamides, polyesters, plasticizers, etc. In one embodiment, the catalytic oxidation of the olefin group can be carried out in a single step using oxygen/ hydrogen peroxide in two-phase reaction employing phase-transfer catalyst. Using the method of the present disclosure, oleic acid can be oxidized to azelaic acid and nonanoic acid.

[0019] The present disclosure thus provides a one step process involving benign reagents. Hydrogen peroxide can be used in stoichiometric amounts, overcoming the issue associated with recycling or disposal of residual hydrogen peroxide. The process can be used for synthesizing diacids from a naturally available fatty acid.

[0020] The present disclosure relates to a method of cleaving oleic acid, and/or derivatives thereof, the method comprising oxidatively cleaving oleic acid, and/or derivatives thereof with oxygen, hydrogen peroxide, tungstic acid as catalyst, methyltrioctylammonium chloride as phase transfer catalyst, and a solvent in an amount from 0 to 30 wt % with respect to the oleic acid, and/or derivatives thereof resulting in the oxidative cleavage of the oleic acid, and/or derivatives thereof. The Applicant has namely found out that working in these conditions allows reaching high yields of azealic and nonanoic acid without using potassium permanganate or an organic solvent and using low amounts of hydrogen peroxide (about the stoichiometric amount).

[0021] In one implementation, the derivatives of oleic acid are salts, and/or esters thereof.

[0022] In one implementation, the tungstic acid catalyst is used in an amount from 1 to 5 mole % with respect to the oleic acid.In one implementation, the hydrogen peroxide to oleic acid molar ratio is in the range from 2:1 to 8:1. In a preferred implementation, the molar ratio of the peroxide compound to oleic acid is about 2:1.

[0023] In one implementation, the solvent may be chosen from polar or non-polar solvents. Non-polar solvents may be chosen in the group constituted by 1,4 dioxane and chloroform. Polar solvents may be chosen from protic solvents like t-butanol, acetic acid, propionic acid and aprotic solvents like acetone, dichloromethane and diglyme. In another implementation, the solvent is t-butanol.

[0024] In one implementation, a solvent is used in an amount from 0 to 10 wt % with respect to the oleic acid.

[0025] In one implementation, the present disclosure relates to a method oxidatively cleaving oleic acid, and/or derivatives thereof with oxygen, hydrogen peroxide, tungstic acid, methyltrioctylammonium chloride, and t-butanol in an amount from 0 to 10 wt % with respect to oleic acid resulting in the oxidative cleavage of the oleic acid, and/or derivatives thereof.

[0026] In one implementation, the present disclosure relates to a method oxidatively cleaving oleic acid, and/or derivatives thereof with hydrogen peroxide, tungstic acid, methyltrioctylammonium chloride, and t-butanol in an amount from 0 to10 wt % with respect to oleic acid with of bubbling of oxygen resulting in the oxidative cleavage of the oleic acid, and/or derivatives thereof.

[0027] The disclosure will now be illustrated with working Examples 1-8 below.

[0028] Example 1 (according to the invention):

Method of cleaving 5g oleic acid:

To a three neck flask fitted with a condenser, dropping funnel and nitrogen inlet were added 5.0 g oleic acid, tungstic acid (2.5 mole % w.r.t oleic acid) and methyltrioctylammonium chloride (brand name Aliquat®336; 2.0 mole % w.r.t oleic acid). Oxygen was bubbled through the reaction mass and temperature was raised to 60°C. Thereafter, hydrogen peroxide (35 %) 2.0 mole/mole of oleic acid was added dropwise and the reaction mass was heated to 80°C for 18 hrs. Reaction mass was extracted with ethyl acetate. After washing organic phase with water it was dried over anhydrous sodium sulphate. Small sample was converted into methyl ester and analyzed by GC. A yield of 72 % for Azelaic acid and a yield of 61 % for nonanoic acid were obtained.

[0029] Example 2 (according to the invention):

Method of cleaving 25g oleic acid:

To a three neck flask fitted with a condenser, dropping funnel and nitrogen inlet were added 25.0 g oleic acid, tungstic acid (2.5 mole % w.r.t oleic acid) and methyltrioctylammonium chloride (brand name Aliquat®336; 2.0 mole % w.r.t oleic acid). Oxygen was bubbled through the reaction mass and temperature was raised to 60°C. Thereafter, hydrogen peroxide (35 %) 2.0 mole/mole of oleic acid was added dropwise and the reaction mass was heated to 75°C for 18 hrs. Reaction mass was extracted with ethyl acetate. After washing organic phase with water, it was dried over anhydrous sodium sulphate. Small sample was converted into methyl ester and analyzed by GC. A yield of 84 % for Azelaic acid and a yield of 71 % for nonanoic acid were obtained.

[0030] Example 3 (according to the invention):

The apparatus described in Example 1 was loaded with the same quantities of reagents except that 30wt % of solvent (t-BuOH) was added. A yield of 72 % for Azelaic acid and a yield of 61 % for nonanoic acid were obtained.

[0031] [0030] Example 4 (comparative Example):

The apparatus described in Example 1 was loaded with the same quantities of reagents except that no methyltrioctyl ammonium chloride is added. Reaction did not take place and azelaic acid and nonanoic acid were not obtained.

[0032] [0031] Example 5 (according to the invention):

The apparatus described in Example 1 was loaded with the same quantities of reagents except that 7.0 wt % of solvent (t-BuOH) was added. Yields of 80 % Azelaic acid and 62 % nonanoic acid were obtained.

[0033] Example 6 (Comparative Example):

Set-up was made same as in Example 1. To 5.0 g oleic acid were added tungstic acid (2.5 mole % w.r.t oleic acid) and methyltrioctylammonium chloride (brand name Aliquat®336; 2.0 mole % w.r.t oleic acid). To this hydrogen peroxide 5.0 mole/mole w.r.t oleic acid was added drop-wise. Yields of 91 % Azelaic acid and 72 % nonanoic acid were obtained.

Table 1 clearly exemplifies that in Example 6 (which is a comparative Example not using oxygen excess hydrogen peroxide as oxidant is required along with phase transfer catalyst. Though the yield is good, the high amount of hydrogen peroxide makes the process uneconomical and also not viable from safety point of view.

[0034] Example 7 (Comparative Example)

The apparatus described in Example 6 was loaded with the same quantities of reagents except that the catalyst tungstic acid was replaced with phosphotungstic acid and 2.0 mole % methyltrioctylammonium chloride was replaced by 6.0 mole % methyltrioctylammonium chloride. Yields of 66.8 % Azelaic acid and 67.4 % nonanoic acid were obtained.

This process was not viable and economical due to high amount of hydrogen peroxide. The reaction was also found to be less effective and the yield was reduced due to replacement of catalyst and high amount of phase transfer catalyst.

[0035] Example 8 (Comparative Example)

Set-up was made same as in Example 1. To 5.0 g oleic acid were added tungstic acid (8.58 mole % w.r.t oleic acid) and 8 ml/g (625 wt %) solvent (t-BuOH). Oxygen was bubbled through the reaction mass and temperature was raised to 60°C. To this hydrogen peroxide 2.0 mole/mole w.r.t oleic acid was added drop-wise. Yields of 93.2 % Azelaic acid and 4.9 % nonanoic acid were obtained.

This process was using the combination of hydrogen peroxide and oxygen as oxidant, thus reducing the amount of hydrogen peroxide. It was however performed in absence of a phase transfer catalyst, thereby requiring an increased amount the catalyst. This yielded azelaic acid in good yield but the yield of nonanoic acid dropped. Further, this process involved usage of high amount of protic solvent, i.e., 625 wt %, which has an inherent disadvantage in that above 75°C the mixture of t-butanol/oxygen vapours enter explosive regime. Therefore, this process, though reducing the amount of hydrogen peroxide required, was still not viable and economical.

The Experimental results are set forth in Table 1 below:

Table 1

Example No	**Substrate**	**Catalyst** (mole %)	**t-Butanol** (ml/g)	**H_2O_2 (30 %)** (m/m)	**O_2**	**Methyltrioctyl ammonium chloride (mole %)**	**Temp.** (°C)	**Time**(hrs)	**Product** (%) [GC]	
									Azelaic	**Nonanoic**
1	Oleic acid* (90 %) **[Reaction done with 5g Oleic]**	H_2WO_4 (2.5)	–	2.0	O_2	2.0	75	18	71.3	60.8
2	Oleic acid (90 %) **[Reaction done with 25g Oleic]**	H_2WO_4 (2.5)	–	2	O_2	2.0	75	18	84.0	71.0
3	Oleic acid* (90 %)	H_2WO_4 (2.5)	30 wt % [0.4 ml/g]	2.0	O_2	2.0	75	18	82	42
4	Oleic acid* (90 %)	H_2WO_4 (2.5)	–	2.0	O_2	–	75	18	nil	nil
5	Oleic acid* (90 %)	H_2WO_4 (2.5)	7.0 wt % [0.08 ml/g]	2.0	O_2	2.0	75	18	80	62
6	Oleic acid (90 %)	H_2WO_4 (2.5)	–	5.0	–	2.0	80	18	91.0	72.0
7	Oleic acid (90 %)	Phospho-tungstic acid (2.5)	–	5.0	–	6.0	80	18	66.8	67.4
8	Oleic acid* (90 %)	H_2WO_4 8.58)	625 wt %	2.0	O_2	–	75	18	93.2	4.9

[0036] The present disclosure thus provides an economical method which is a one-step process involving benign reagents. Hydrogen peroxide is used in equivalent (stoichiometric) proportion, overcoming the issue of recycling or disposal of residual hydrogen peroxide.

[0037] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Claims

1. A method of cleaving oleic acid and/or at least one derivative thereof, the method comprising:

oxidatively cleaving oleic acid and/or the derivative thereof in a reaction medium comprising the oleic acid and/or derivative thereof, oxygen, hydrogen peroxide, tungstic acid as catalyst, methyltrioctylammonium chloride as phase transfer catalyst, and a solvent in an amount from 0 to 30 wt % with respect to the oleic acid and/or the derivative thereof.

2. The method as claimed in claim 1, wherein the derivative of oleic acid is selected from the group consisting of salts and esters.

3. The method as claimed in any of claims 1 or 2, wherein the catalyst is used in an mont from 1 to 5 mole % with respect to the oleic acid, and/or derivatives thereof.

4. The method as claimed in any of claims 1 to 3, wherein the hydrogen peroxide to oleic acid molar ratio is in the range from 2:1 to 8:1.

5. The method as claimed in any of claims 1 to 4, wherein the solvent is selected from the group consisting of t-butanol, chloroform, acetic acid, propionic acid, 1, 4-dioxane, diglyme, and/or combinations thereof.

6. The method as claimed in any of claims 1 to 5, wherein the solvent is used in the range from 0 to 10 wt % with respect to the oleic acid, and derivatives thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/081321

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C51/16
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, WPI Data, BIOSIS, COMPENDEX, EMBASE, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/092353 A1 (DSM IP ASSETS BV [NL]) 27 June 2013 (2013-06-27) the whole document, in particular examples and claims	1-6
A	CN 104 447 279 B (UNIV LIAONING SHIHUA) 18 May 2016 (2016-05-18) cited in the application	1-6
A	CN 1 680 253 A (XINJIANG PHYSICAL AND CHEMICAL [CN]) 12 October 2005 (2005-10-12)	1-6

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ANTONELLI ERMANNO ET AL: "Efficient Oxidative Cleavage of Olefins to Carboxylic Acids with Hydrogen Peroxide Catalyzed by Methyltrioctylammonium Tetrakis(oxodiperoxotungsto)phospate(3-9 under Two-Phase Conditions. Synthetic Aspects and Investigation of the Reaction Course", THE JOURNAL OF ORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY, US, vol. 63, 1 January 1998 (1998-01-01), pages 7190-7206, XP002142961, ISSN: 0022-3263, DOI: 10.1021/JO980481T -----	1-6
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/081321

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