

NON LINEAR ALIPHATIC PEROXY CARBOXYLIC
ACID PRECURSORS

5

Field of the Invention

This invention relates to the field of oxidisable stain removal, especially but not solely to the removal of oxidisable stains from fabrics and is particularly concerned with the
10 removal of these stains using peroxygen bleaches at temperatures $\leq 60^{\circ}\text{C}$ such as are encountered in domestic washing and laundering operations.

Background to the Invention

The removal of oxidisable stains from either hard surfaces
15 or fabrics by means of peroxygen bleaches at temperatures less than 60°C is a well known technique and customarily involves the use of organic peroxy acids. the most commonly used peroxy acid is peracetic acid, normally generated in situ in the bleaching or laundry liquor by the reaction of alkaline hydrogen peroxide
20 with a peroxy acid precursor (the so-called bleach activator). However, peroxyacids containing more than 2 carbon atoms in the acyl group have also been disclosed and taught for this purpose and BP 864,798, Canadian Patent No. 635,620, US Patent Nos. 4100095, 4119660, 4126573 and European Published Application

No. 0068547 all relate to the formation, stabilisation or use of such materials.

5 Recently, as described in European Application No. 0068547, it has been found that selection of the chainlength of the aliphatic moiety of the peroxy acid permits the peroxy acid to be concentrated in the area where stain removal is required. Thus for removal of fugitive dyestuffs in bulk solution, a 'hydrophilic' bleach species is satisfactory, whereas for stains on solid surfaces a bleaching species
10 showing more hydrophobic character, and hence a tendency to migrate to the solid-liquid interface, may be more beneficial.

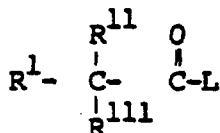
In the commonly assigned US Patent No. 4412934 issued to Stanley Y Chung & Gianfranco L Spadini, on November 1st 1983 entitled "Bleaching Compositions", and Published European
15 Application No. 0098129 entitled "Detergent Additive Product" compositions are disclosed which incorporate a C_8-C_{10} acyloxy compound capable of forming a C_8-C_{10} aliphatic peroxy acid on reaction with alkaline hydrogen peroxide, the C_8-C_{10} acyl group being linear in nature.

20 Although compositions prepared in accordance with these last named disclosures provide superior stain removal performance to prior art products employing peracetic acid or its precursors, it has been found that, under certain conditions, odours produced in the wash solution by these
25 products are aesthetically unattractive.

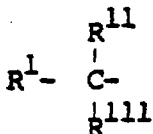
It has now been found that certain non-linear aliphatic peroxy acid precursors, when added to aqueous liquors containing a source of alkaline hydrogen peroxide, provide effective bleaching of oxidisable stains,
30 particularly at temperatures at or below 60°C without generating aesthetically unattractive odours. The precursor compounds can be added to such liquors on their own, or added to water as part of a complete inorganic peroxy
35 bleach-containing detergent composition or as part of a laundry additive product added to an aqueous solution of an inorganic peroxy bleach-containing detergent composition.

Summary of the Invention

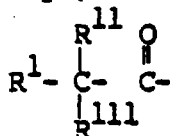
According to the invention therefore there is provided a non linear aliphatic peroxydicarboxylic acid precursor adapted to form a non linear aliphatic peroxy acid in aqueous alkaline hydrogen peroxide solution wherein the precursor has the general formula:



wherein the group:



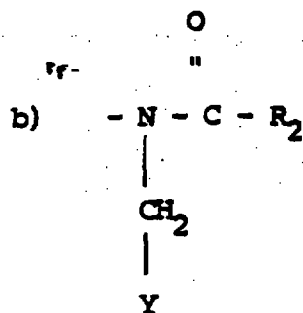
is an aliphatic hydrocarbyl organic moiety of non linear structural configuration, at least one of R^{II} and R^{III} being hydrogen, the other of R^{II} and R^{III} being independently selected from hydrogen and C_1 - C_4 alkyl groups, the group:



containing at least five carbon atoms in a linear chain extending from and including the carbonyl carbon and being the acyl moiety of a carboxylic acid having a $\log P_{oct}$ of from 1.9 to 4.1, wherein P_{oct} is the partition coefficient of the carboxylic acid between n-octanol and water at 21°C, and L is a leaving group selected from:

a)





wherein R_2 is an alkyl group containing from 1 to 4 carbon atoms, x is 0 or an integer from 1 to 4 and Y is selected from:

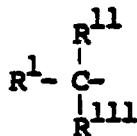
- SO_3M
- OSO_3M
- CO_2M
- $\text{N}^+(\text{R}_2)_3\text{Q}^-$
- $\text{N}(\text{R}_2)_2\text{O}$

wherein M is H, alkali metal, alkali earth metal ammonium or substituted ammonium and Q is a halide or methosulphate the conjugate acid of said leaving group L having a pKa in the range from 6 to 13.

These leaving groups have a pKa more preferably in the range from 7 to 11, most preferably from 8 to 10.

Preferred leaving groups are those of formula a) above in which x is 0 and Y is selected from $-\text{SO}_3\text{M}$ and $-\text{CO}_2\text{M}$ wherein M is alkali metal preferably sodium.

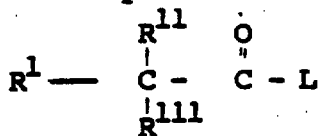
Preferably the group:



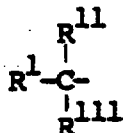
5 is a C₇-C₉ alkyl group and preferred compounds are alkali metal, ammonium or substituted ammonium 2-ethyl hexanoyl oxybenzene sulphonates and 3,5,5-trimethyl hexanoyl oxybenzene sulphonates, with sodium being the preferred cation.

Detailed Description of the Invention

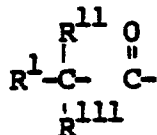
The compounds found to be useful as organic peroxyacid bleach precursors have the formula



wherein the group:



- 15 is an aliphatic hydrocarbyl organic moiety of non linear structural configuration, at least one of R^{ll} and R^{lll} being hydrogen, the other of R^{ll} and R^{lll} being independently selected from hydrogen and C_1 - C_4 alkyl groups, the group:



containing at least five carbon atoms in a linear chain extending from and including the carbonyl carbon and

- 20 being the acyl moiety of a carboxylic acid having a $\log P_{\text{oct}}$ of from 1.9 to 4.1, wherein P_{oct} is the partition coefficient of the carboxylic acid between n-octanol and water at 21°C, and L is a leaving group the conjugate acid of which has a pKa in the range from 6 to 13.

R^I is an aliphatic hydrocarbyl organic moiety which can be linear, branched or cyclic.

5 The effects of structure on the hydrophobicity of organic compounds as represented by their partition coefficients between octanol and water are described by A Leo et al in Chemical Reviews, 71, pp 525-616 (1971). The authors provide numerical values for the change in $\text{Log}P_{\text{OCT}}$ (where P_{OCT} is the partition coefficient between n-octanol and water) 10 associated with the incorporation of various substituents into a range of structures. This permits a value for $\text{Log}P_{\text{OCT}}$ to be predicted for any structure.

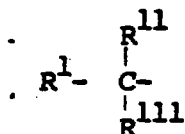
All of the compounds display surface activity but this property is not very marked for compounds in which the group 15 $R^I-C(R^{II}R^{III})-$ contains less than 8 carbon atoms and only those compounds in which $R^I-C(R^{II}R^{III})-$ contains more than 10 carbon atoms display detergent characteristics. Hydrocarbyl group branching confers increased solubility relative to linear compounds of the same number of carbon 20 atoms and this increased solubility is associated with a decrease in surface activity relative to the corresponding linear compound. This effect also holds true for the aliphatic peroxy acids produced on perhydrolysis of the compounds. However, it has now surprisingly been found that 25 aqueous liquors containing non linear aliphatic peroxy

carboxylic acids in which non linearity preferably occurs on the 2- and/or 3-carbon atoms with respect to the carbonyl carbon have a less intense odour of more aesthetically acceptable character than those containing the corresponding linear aliphatic peroxyacids. The latter characteristically have intense, pungent, and aesthetically unattractive odours which are difficult to mask using conventional detergent fragrances.

The existence of non linearity on carbon atoms further removed from the carbonyl carbon than the 3-carbon atom position also appears to be beneficial but to a lesser extent and little or no odour benefit is seen for non linearity commencing at 5- or higher carbon atom positions relative to the carbonyl carbon. Accordingly, branching on 5- and higher carbon atoms is not believed to be critical to the odour forming capability of the compound. The reason for this difference in behaviour between branched and linear aliphatic peroxy acids is not well understood and does not appear to be predictable.

The introduction of non linearity into the organic group $R^1-C(R^{II}R^{III})-$ also affects the rate of perhydrolysis of the precursor in alkaline hydrogen peroxide solutions. Substitution and, in particular, di substitution of an alkyl group on the 2-carbon causes a lowering in the rate of perhydrolysis of the precursor because it hinders the approach of perhydroxyl ion and is believed to reduce the effectiveness of the percarboxylic acid as a bleach. Compounds in accordance with the invention should therefore have at least one hydrogen atom on the 2-carbon atom. Non linearity on the 2-carbon is less preferred than on the 3-carbon where e.g. di alkyl substitution has much less effect on the perhydrolysis of the compound whilst still providing an aliphatic peroxy acid of improved odour.

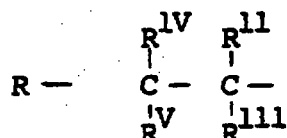
One preferred form of the group:



wherein R^{11} and R^{111} are as previously defined, is thus the group:



5 R^{1V} and R^V are each independently selected from hydrogen and C_1-C_4 alkyl groups and the group:

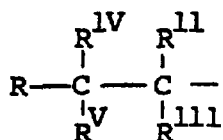


10 comprises a C_6-C_{16} alkyl group in which at least one of R^{11} R^{111} R^{1V} and R^V are C_1-C_4 alkyl, there being a linear chain of five or more carbon atoms extending from and including the carbonyl carbon. Preferably R^{11} and R^{111} are hydrogen atoms.

Branched chain alkyl group-containing precursors in which there is no more than a single branch on the 2-carbon but at least one on the 3-carbon perhydrolyse at an adequate rate

(i.e. $\geq 80\%$ conversion within approximately 5 minutes) but still produce an odour when dissolved in an aqueous alkaline solution of hydrogen peroxide. However this odour is of a more acceptable type and level than that produced by the corresponding linear alkyl precursors under the same conditions.

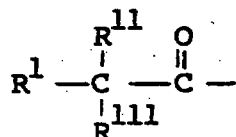
A preferred number of carbon atoms in the alkyl group:



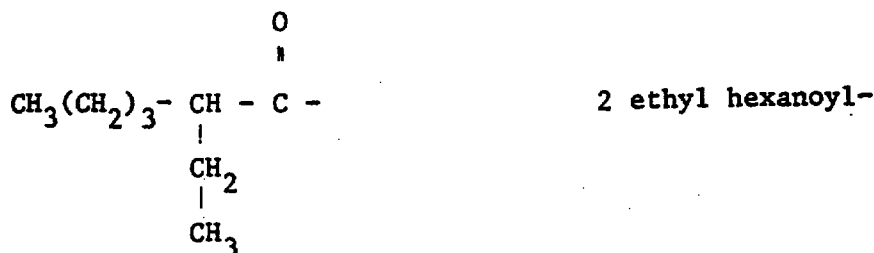
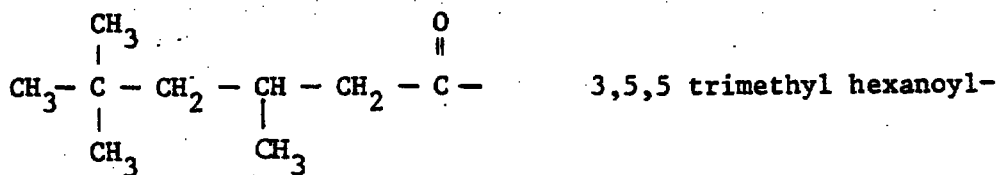
is from 7 to 9 carbon atoms with a linear chain of from 5 to 8 carbon atoms and with R^{IV} and/or R^{V} comprising a side chain i.e. in the 3-carbon position with respect to the carbonyl carbon atom.

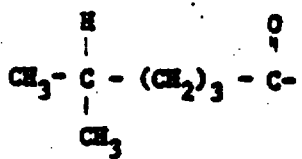
The most preferred R group structures of this type are C_7 - C_9 radicals in which there is a single methyl side chain in the 3-carbon atom position and the alkyl group is terminated by a tertiary butyl moiety.

Structures in accordance with the invention for the group

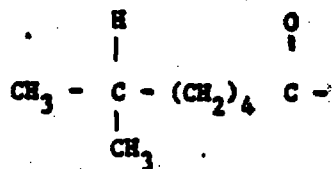


where R^{I} is aliphatic include:





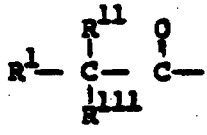
5-methyl hexanoyl-



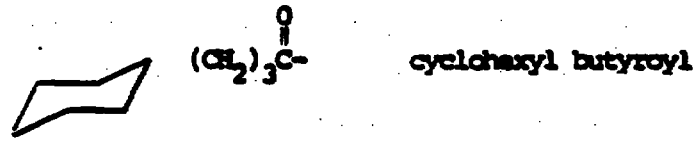
6-methyl heptanoyl-

Of the above the 3,5,5 trimethyl hexanoyl structure is the most preferred for odour and rate of perhydrolysis with the 5-methyl hexanoyl and 6-methylheptanoyl structures being less preferred for odour and the 2-ethyl 5 hexanoyl being less preferred for the rate of perhydrolysis.

An example of a structure in accordance with the invention for the group



where R^{I} incorporates a cyclo aliphatic functionality is

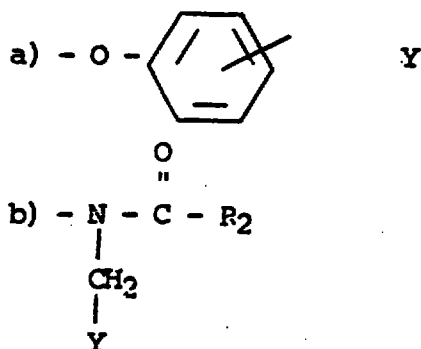


The leaving group L must be capable of displacement from the bleach precursor as a consequence of the nucleophilic attack on the bleach precursor by perhydroxyl anion generated by alkaline hydrogen peroxide. This, the perhydrolysis reaction, results in the formation of the percarboxylic acid. Generally, for a group to be a suitable leaving group it must exert an electron withdrawing effect within the precursor molecule as this facilitates the nucleophilic displacement by the perhydroxyl anion.

Suitable leaving groups for this purpose have conjugate acid forms, the pKa of which should lie within the range from 6 to 13. pKa values above 13 make the electron withdrawal effect so small as to be ineffective in promoting nucleophilic attack by perhydroxide anion, an example of such a leaving group being $-OCH_3$. pKa values below 6 reflect such a large electron withdrawal effect as to make the molecule reactive to a wide variety of materials including e.g. water. Certain aliphatic anhydrides fall into this class. Preferred leaving groups have a pKa in the range from 7 to 11, more preferably from 8 to 10.

However for the purposes of the present invention the leaving group must also confer a degree of solubility on the precursor molecule so that it partitions between the aqueous phase and any organic phase present. Certain leaving groups such as sulphonamide groups, having conjugate acid forms of the appropriate pKa, do not provide sufficient aqueous solubility to the precursor molecule and therefore do not give a sufficient rate of perhydrolysis to be practicable in a laundry detergent liquor.

The leaving groups L found to be useful in compounds of the present invention are those having the formula



wherein R_2 is an alkyl group
containing from 1 to 4 carbon atoms;

and Y is selected from:

- SO_3M
- OSO_3M
- CO_2M
- $\text{N}^+(\text{R}_2)_3\text{Q}^-$
- $\text{N}(\text{R}_2)_2\text{---O}$

wherein M is H, alkali metal, alkali earth metal ammonium or
substituted ammonium; and Q is halide or methosulphate.

The preferred leaving group L has the formula a) in which
Y is a sulphonate, or carboxylate.

The position of the solubilising group Y on the benzene
ring in formula a) is not critical in that o-, m- and
p-positions provide operable species. Nevertheless polar and
steric factors make the o-substituted material most difficult
to synthesise and of least value in that steric hindrance
impedes the approach of perhydroxyl ion. In the preferred
embodiment of leaving group L, where Y is a sulphonate
radical, the precursor will normally be isolated in the form
of its alkali metal salt because of the difficulty of
handling the acid form.

Synthesis of the compounds of the invention can be
illustrated generally by a sequence of reactions in which a
 $\text{C}_7\text{---C}_{17}$ acid or acid chloride is formed in which the acyl
group has the required branched structure and the subsequent
reaction of this with a compound of formula a) above wherein
the free bond is satisfied by a hydrogen atom.

The $\text{C}_7\text{---C}_{17}$ acid or acid chloride starting material,
in which the acyl group has a linear chain of at least 5
carbon

atoms extending from and including the carbonyl carbon and including a branch in at least the 2- and/or 3-carbon position, is prepared by methods known in the art.

Thus modified OXO syntheses can be used in which
5 alpha-olefins are reacted with carbon monoxide and water in the presence of cobalt catalysts to form a mixture of acids of which 60-65% have either 2-methyl or 2-ethyl branching. If branched olefins are used as the starting material, the resulting acids are completely branched. Branched olefins
10 themselves, having chain lengths up to C₁₅, are produced by polymerising propylene or butene using a phosphoric acid catalyst under conditions of high temperature and pressure. The dimerisation of isobutene or the codimerisation of
15 n-butene and isobutene leads to a highly branched isononanoic acid which is a preferred starting material. The olefin source for another preferred starting material, 2-ethyl hexanoic acid, is propylene, which is converted to n-butyraldehyde and thence to 2-ethyl hexanoic acid by aldol condensation of the aldehyde followed by hydrogenation of the
20 aldol condensation product and final oxidation.

Manufacture of the acid reactant used in the preparation of sodium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate, a preferred compound in accordance with the invention, involves the condensation of two moles of butene to form diisobutene
25 followed by carbonylation to produce the aldehyde and subsequent oxidation to form the isononanoic acid. This is then converted into the acid chloride in known manner. The acid chloride is refluxed with sodium phenol sulphonate in a nitrogen current at 100-150°C for 10-20 hours to form the
30 sodium 3,5,5-trimethyl hexanoyl benzene sulphonate. Alternatively, the isononanoic acid can be transesterified, refluxing at 160-180°C with sodium phenol sulphonate and acetic anhydride in the presence of a small amount of sodium acetate catalyst, thereafter volatilising the by-product
35 acetic acid and precipitating the sulphonate salt product from an organic solvent. A similar reaction procedure starting with n-nonanoic acid is disclosed and claimed in the Published European Patent Application No. 0105672.

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19.62 gms of finely powdered, anhydrous sodium phenol
sulphonate (1/10th mole) and 22.06 gms of Akzo
isononanoyl chloride (weight 1/10th mole + 25% excess)
were weighed into a 500 ml conical flask containing 250
5 mls of chlorobenzene. The flask was fitted with a
magnetic stirrer, a 2-way head carrying a N₂ gas inlet
(leading to the base of the flask) and a reflux condenser
(+ CaCl₂ tube) and was surrounded by an oil-bath. The
flask was heated with stirring to 120°C and with N₂ gas
10 passing through the flask, was maintained at that
temperature overnight (20 hours). The heating was then
turned off and the flask contents allowed to cool to room
temperature. The contents were then washed with 3 x 1
litre diethyl ether, filtering between each wash (a
15 ^(RTM) Silverson stirrer was used for agitation). The resulting
white solid was dried in a vacuum oven (no heat) after
which the product was ground into a fine powder and dried
again in the vacuum oven.

Yield: 27.40 gms (81.5% yield)

20 NMR analysis showed 81.4% required compound.

2) Synthesis of sodium 2-ethyl hexanoyl oxybenzene sulphate

Anhydrous sodium phenol sulphate (58.85g; 0.3 mole) was added to a stirred mixture of acetic anhydride (36.75g; 0.36 mole), 2-ethylhexanoic acid (129.8g; 0.9 mole) and sodium acetate (3g). The resultant white suspension was stirred under nitrogen and heated to 160°C under reflux; vigorous boiling occurred and was maintained for 4.5 hours.

At this point the nitrogen lead was transferred from the condenser top to a spare inlet on the flanged-top of the reaction vessel and the condenser was set up in a distillation mode. The pot temperature was gradually increased to 260°C during 1.5 hours; the still-head temperature rose to 131°C. The contents of the reaction pot were then allowed to cool overnight to ambient temperature before being washed with 3 x 1.5 litres diethyl ether, filtering between washes, and then being dried.

The yield of sodium 2-ethyl hexanoyl oxybenzene sulphate was 88.3g, 91.3% of theory.
Purity (by cat. SO₃ determination) = 93.4%.

The compounds of the invention, as defined above, find their principal application in detergent compositions primarily as peroxyacid bleach precursors, (the so-called low temperature bleach activators). Such detergent compositions comprise an organic surfactant, a compound as hereinbefore defined and a source of alkaline hydrogen peroxide and are normally particulate in physical form.

The peroxyacid precursors of the present invention can also be incorporated into detergent additive products.

Such additive products are intended to supplement or boost the performance of conventional detergent compositions and may contain any of the components of such compositions, although they will not comprise all of the components present in a fully formulated detergent composition.

Such additive products may comprise the compound alone in combination with a carrier such as a compatible particulate substrate, a flexible non particulate substrate or a container.

The present invention also finds utility in the formation of aqueous bleaching liquors by means of the reaction of a source of alkaline hydrogen peroxide with a precursor of an aliphatic peroxy acid whose carboxylic acid analogue has a log P_{OCT} of from 1.9 to 4.1 particularly with the C_6-C_{16} branched alkyl group-containing precursor compounds specifically described above, or by means of the addition of the above-described detergent or bleaching compositions to an aqueous medium. Aqueous bleaching liquors containing the most highly preferred compounds in accordance with the invention are virtually odourless whereas the analogous linear alkyl chain materials have a pungent odour which is aesthetically undesirable. Such bleaching liquors and the detergent compositions and additive products employed in their production are the subject of the copending Divisional Application Publication No. 2175928A.

EXAMPLE 1

Preparation of sodium 3,5,5 trimethyl hexanoyl oxybenzene sulphate

100 gms of dehydrated sodium phenol sulphate and 117
 5 gms. (30% molar excess) of isononanoyl chloride* (ex Akzo BV,
 Mwt 176.5) were weighed into a 2 litre conical flask. The
 flask was fitted with magnetic stirrer and carried a 2-way
 head fitted with an Airflux condenser and a nitrogen inlet
 tube leading to the base of the flask. 500 mls chlorobenzene
 10 were added and the resulting suspension was stirred. 5 gms
 of tetrabutylammonium bromide (supplied by Aldrich Chemical
 Co. Inc., Milwaukee, Wisconsin 53233, USA) were added as
 catalyst and the resulting suspension was stirred and heated
 to 120°C with nitrogen passing through the flask. Heating
 15 was continued with nitrogen passing, for 19.5 hours.

The reaction mixture was then cooled to room temperature,
 poured into 3 litres of diethyl ether and well washed using a
 Silverson stirrer. The solid material was filtered off by
 Buchner filtration and the resulting solid was washed with
 20 2x2 litres of ether, filtering off after each wash. The
 resulting solid was dried over P_2O_5 in a vacuum
 desiccator, was powdered in a coffee grinder and re-dried in
 a vacuum desiccator over P_2O_5 . The yield was 140 gms and
 NMR analysis showed the solid to comprise 92% sodium 3,5,5
 25 trimethyl hexanoyl oxybenzene sulphate and 8% sodium phenol
 sulphate.

*This is the common term used in the trade to describe 3,5,5
 trimethyl hexanoyl chloride.

EXAMPLE 2

30 Preparation of sodium 3,5,5 trimethyl hexanoyl oxybenzoic acid

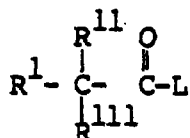
The same apparatus was used as in Example 1. 74.5 g of
 p-hydroxybenzoic acid was mixed with 100g of 3,5,5-trimethyl

5 hexanoyl chloride (5% molar excess) and 3.7 g of tetrabutyl ammonium bromide catalyst. The mixture was stirred and heated to 100°C in a current of nitrogen for 2 hours. The resultant white, porous, solid mass was cooled, broken up under petroleum ether (bp 40-60°C), filtered, washed and dried. The product, 126 g (84%) was found by NMR analysis to be 95% 3,5,5-trimethyl hexanoyl oxybenzoic acid and 5% p-hydroxy benzoic acid.

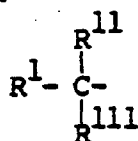


CLAIMS

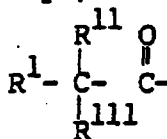
1. A non-linear aliphatic peroxydicarboxylic acid precursor adapted to form a non-linear aliphatic peroxy acid in aqueous alkaline hydrogen peroxide solution characterised in that the precursor has the general formula:



5 wherein the group:



is an aliphatic hydrocarbyl organic moiety of non linear structural configuration, at least one of R^{II} and R^{III} being hydrogen, the other of R^{II} and R^{III} being independently selected from hydrogen and C_1 - C_4 alkyl groups, the group:



10 containing at least five carbon atoms in a linear chain extending from and including the carbonyl carbon and being the acyl moiety of a carboxylic acid having a $\log P_{oct}$ of from 1.9 to 4.1, wherein P_{oct} is the partition coefficient of the carboxylic acid between n-octanol and water at 21°C, and L is a leaving group selected from:

a)



O

"

b) $-N-C-R_2$

CH_2

Y

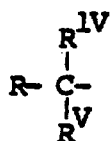


wherein R_2 is an alkyl group containing from 1 to 4 carbon atoms, x is 0 or an integer from 1 to 4 and Y is selected from:

- SO_3M
- OSO_3M
- CO_2M
- $N^+(R_2)_3Q^-$
- $N(R_2)_2O$

- wherein M is H, alkali metal, alkali earth metal ammonium or substituted ammonium and Q is a halide or methosulphate the conjugate acid of said leaving group L having a pKa in the range from 6 to 13.

2. A non linear aliphatic peroxycarboxylic acid precursor according to claim 1 characterised in that R^1 comprises the group:



- 5 wherein R^{IV} and R^V are each independently selected from hydrogen and C_1-C_4 alkyl groups, and the group :



comprises a C_6-C_{16} alkyl group in which at least one of R^{II} , R^{III} , R^{IV} and R^V are C_1-C_4 alkyl, there being a linear alkyl chain of five or more carbon atoms extending from and including the carbonyl carbon.

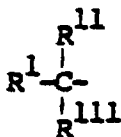


3. A non linear aliphatic peroxy-carboxylic acid precursor according to either one of claims 1 and 2 wherein:



is a C_6-C_{12} group wherein R^{11} and R^{111} are hydrogen atoms.

- 5 4. A non linear aliphatic peroxy-carboxylic acid precursor according to claim 3 wherein:



is a C_7-C_9 group.

- 10 5. A compound according to any one of claims 1-4 wherein the conjugate acid of leaving group L has a pKa in the range from 7 to 11.

6. A compound according to claim 5 wherein L has the formula
a) in which x is 0 and Y is $-SO_3M$ or $-CO_2M$.

7. An alkali metal ammonium or tri C_2-C_3 alkanolammonium 2-ethyl hexanoyl oxybenzene sulphonate.

- 15 8. An alkali metal ammonium or tri C_2-C_3 alkanolammonium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate.

9. 2-ethyl hexanoyl oxybenzoic acid and alkali metal, alkaline earth metal, ammonium and tri C_2-C_3 alkanolammonium salts thereof.



10. 3,5,5,trimethyl hexanoyl oxybenzoic acid and alkali
metal, alkaline earth metal, ammonium and tri C₂-C₃
alkanol ammonium salts thereof.
