607844

COMMONWEALTH of AUSTRALIA
Patents Act 1952

APPLICATION FOR A STANDARD PATENT

I/We

Rhone-Poulenc Chimie

of

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 11.12.90 LS

25 Quai Paul Doumer, 92408 Courbevoie, France

hereby apply for the grant of a Standard Patent for an invention entitled:

Process for the catalytic oxidation of alkanes to mixtures of alcohols and ketones

which is described in the accompanying complete specification.

Details of basic application(s):-

Number	Convention Country	Date
8802987	France	3 March 1988

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this SECOND day of MARCH 1989

To: THE COMMISSIONER OF PATENTS

Keith L Leslie
.....
a member of the firm of
DAVIES & COLLISON for
and on behalf of the
applicant(s)

M007069 02/03/89

Davies & Collison, Melbourne

COMMONWEALTH OF AUSTRALIA R-5

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

In support of the Application made for a patent for an invention

Insert title of invention.

entitled: "PROCESS FOR THE CATALYTIC OXIDATION OF ALKANES TO MIXTURES OF ALCOHOLS AND KETONES"

Insert full name(s) and address(es) of Declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I Monique VARNIERE-GRANGE -Ingenieur-Brevets

~~We~~

of: RHONE-POULENC CHIMIE, a French Body Corporate, of: 25, quai Paul Doumer, 92408 COURBEVOIE, France.

Cross out whichever of paragraphs 1(a) or 1(b) does not apply.

1(a) relates to application made by individual(s).

1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows :-

~~I am / We are~~ the applicant for the patent

or (b) I am authorized by

RHONE-POULENC CHIMIE

the applicant ~~S~~ for the patent to make this declaration on ~~their~~ its behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply.

2(a) relates to application made by inventor(s)

2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

~~I am / We are~~ the actual inventor of the invention

or (b) MICHEL COSTANTINI and JEAN-PIERRE LECOMTE,

of: 10, rue du Docteur Bonhomme, 69003 LYON, France and 24, rue Boileau, 69006 LYON, France respectively.

~~is / are~~ the actual inventor ~~S~~ of the invention and the facts upon which the applicant ~~S~~ ~~is / are~~ entitled to make the application are as follows :-

State manner in which applicant(s) derive title from inventor(s)

"The applicant would, if a patent were granted upon an application made by the Inventors, be entitled to have the patent assigned to it"

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ~~was~~ made

in FRANCE NO. 88/02 987 on the 3rd March, 1988

by RHONE-POULENC CHIMIE

in ..... on the .....

by .....

in ..... on the .....

by .....

4 The basic application..... referred to in paragraph 3 of this Declaration ~~was~~ the first application..... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at St-FONS this 4 day of Janvier 1989

Signature of Declarant(s) (no attestation required).

RHONE-POULENC CHIMIE FIN
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Note: Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-30941/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 607844

(54) Title
PROCESS FOR THE CATALYTIC OXIDATION OF ALKANES TO MIXTURES OF ALCOHOLS AND KETONES

International Patent Classification(s)
(51)[4] C07C 027/16 C07C 029/48 C07C 045/29 C07C 045/53
(51)[5] C07C 045/28

(21) Application No. : 30941/89 (22) Application Date : 02.03.89

(30) Priority Data

(31) Number	(32) Date	(33) Country
88 02987	03.03.88	FR FRANCE

(43) Publication Date : 07.09.89

(44) Publication Date of Accepted Application : 14.03.91

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(56) Prior Art Documents
US 3879467
US 4203926
US 3928452

(57) Claim

1. Process for the oxidation of an alkane with an organic hydroperoxide to produce a mixture of alcohols and ketones, which comprises contacting a said alkane and a said hydroperoxide at a temperature above 20°C in the presence of a catalytic quantity of osmium or an osmium compound.

607844

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

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This document contains the amendments made under Section 49 and is correct for printing

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Michel COSTANTINI
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1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

Process for the catalytic oxidation of alkanes to mixtures of alcohols and ketones

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

The present invention relates to the catalytic oxidation of alkanes to mixtures of alcohols and ketones.

The catalytic oxidation of alkanes with organic hydroperoxides is known and various catalytic systems for this reaction have already been proposed.

Thus, D. Mansuy et al. in Angew. Chem. Int. English Edition 19 (1980) No 11, 909-910 described the decomposition of cumyl hydroperoxide in cyclohexane at 20°C, in which the catalyst is the Os(TPP)(CO)(pyridine) complex where TPP designates tetraphenylporphyrin. However, the yield of required products (cyclohexanol and cyclohexanone) is insignificant and the activity of the catalyst is very low. Moreover if its structure is modified at 20°C, work carried out by the Applicant shows that it is destroyed at a higher temperature. In these conditions, development of such a technique on an industrial scale using a complex of prohibitive cost is greatly impaired.

Moreover French Patent Application No. 2 559 254 describes in particular the oxidising deperoxidation of t-butyl and cumyl hydroperoxides in cyclohexane or octane in which the catalyst is cobalt complex carrying in particular at least one ligand having a bis(2'-pyridylimino)-isoindoline skeleton. It is also shown by Example 27 of the said Application that the compound $Co(Oct)_2$ whose structure is simpler and which does not carry a ligand of the above indicated type only exhibits very poor efficiency.

That Application mentions the possible replacement of cobalt, the central metal in the complexes in question, by any other metal of Group VIII, osmium being one of the possibilities considered. However the ligands in question are relatively difficult to prepare and the efficiency of the set of complexes tested in the reaction under consideration, whose central metal is cobalt, remains poor. Development of such a technique on an industrial scale is hence also impaired.

It was hence necessary to propose a process for the catalytic oxidation of alkanes by organic hydroperoxides which is more efficient and which allows the use of catalysts that are more stable to heat, more readily accessible and which can be recycled if necessary.

The present invention provides a process for the oxidation of alkanes with organic hydroperoxides to mixtures of alcohols and ketones at a temperature above 20°C and in the presence of a catalytic quantity of osmium or a compound of osmium.

The alkane substrate of the present process may be a saturated hydrocarbon of formula:

RH (I)

in which R represents:

- a linear or branched alkyl group having 1 to 30 carbon atoms,

- a cycloalkyl group having 3 to 12 carbon atoms in the ring, optionally substituted by one or more alkyl groups

containing up to 4 carbon atoms each,

- a polycycloalkyl group having 2 to 5 rings each of which may contain 3 to 12 carbon atoms, or

- an alkyl- or cycloalkyl-aromatic group having 7 to 30 carbon atoms.

More specifically R may represent:

- a linear or branched alkyl group having 1 to 12 carbon atoms,

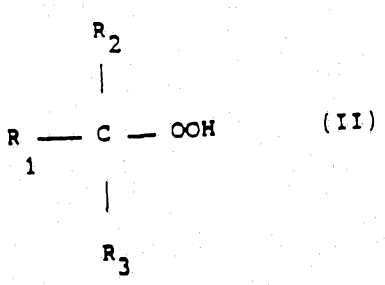
- a cycloalkyl group having 5 to 12 carbon atoms in the ring,

- an alkylbenzene residue in which the alkyl group contains up to 4 carbon atoms, or

- a cycloalkylbenzene residue in which the cycloalkyl group contains 5 to 8 carbon atoms.

Examples of oxidisable alkanes which can be used in the present process are methane, ethane, propane, isobutane, isopentane, butane, hexane, octane, cyclopentane, cumene, toluene, tetralin, decalin, cyclododecane and pinane.

The organic hydroperoxide used in the present process may be represented by the formula:



(II)

in which:

- R_1 to R_3, which may be the same or different, each represent:

hydrogen,

a linear or branched alkyl of 1 to 30 carbon atoms,

a cycloalkyl group having 3 to 12 carbon atoms,

an alkyl- or cycloalkyl-aromatic group having 7 to 30 carbon atoms, or

an aryl group, optionally substituted by one or two alkyl groups containing up to 4 carbon atoms each or aryl groups having 6 to 20 carbon atoms each;

- two of the groups R_1 to R_3 may together form a single divalent alkylene radical of 4 to 10 carbon atoms.

More specificially R_1 to R_3, which may be the same or different, each represent:

alkyl of 1 to 4 carbon atoms,

phenyl, or

two of them together may represent a divalent radical forming with the carbon atom to which it is attached a cyclohexyl or cyclooctyl residue, and not more than one of them may represent a hydrogen atom.

As examples of organic hydroperoxides suitable for carrying out the present invention one may mention tertiary butyl hydroperoxide, cumyl hydroperoxide, cyclohexyl hydroperoxide and ethylbenzene hydroperoxide.

The present process produces a mixture containing at least the alcohol and at least the ketone corresponding to the alkane used as starting material or to the alkyl part of the aralkyl substrate. Thus from cyclohexane a mixture of cyclohexanol and cyclohexanone commonly referred to as OLONE will be obtained, which are useful intermediates in various manufacturing processes (eg for adipic acid and caprolactam). In the same way starting from ethylbenzene a mixture of 1-phenylethanol and acetophenone will be obtained, useful for the manufacture of styrene.

The performance of the present process requires the presence of osmium or of a compound of osmium.

Any source of osmium may be used in the context of the present invention. The osmium may, indeed, be involved in metallic form, if necessary, finely divided or deposited on a support such as activated charcoal. Also suitable for the performance of the said process are compounds of osmium in which the osmium has a zero degree of oxidation such as triosmium dodecacarbonyl. Inorganic compounds of osmium may also be used in which the osmium exhibits any degree of oxidation from 2 to 8. As examples of such compounds one may mention: OsO, Os_2O_3, OsO_2, OsO_4, $OsCl_3$, K_2OsO_4, $NaOsF_6$, $OsOCl_4$, $K_2OsO_4(OH)_2$, $OsCl_4$ and $OsOF_5$.

It is also possible to use organic compounds of osmium or osmium complexes such as tetracyclohexyl osmium, tetra(cyclohexyloxy) osmium or the Os(TPP)(CO)-(pyridine) complex and particularly, complexes carrying ligands with a high nitrogen atom density (e.g. tri- or tetranitrogenated) like the ligands exhibiting the tetraphenylporphyrin skeleton. Most of the complexes in question release an inorganic form of osmium in situ in the conditions of the reaction either by degradation of the ligands or by decomplexation.

Preferably, the form of osmium used will be any one of the following group:

Os/C, $Os_3(CO)_{12}$, OsO, Os_2O_3, OsO_2, OsO_4 and $OsCl_3$.

Osmium tetroxide is particularly suitable for the performance of the invention.

The quantity of osmium to be involved is not critical and may vary within wide limits. For good performance of the invention it will be at least 10^{-6} mole of osmium per mole of hydroperoxide and there is no observable advantage in exceeding a quantity of 10^{-1} mole of osmium per mole of hydroperoxide. This quantity is, preferably, between 10^{-2} and 10^{-5} mole of osmium per mole of hydroperoxide.

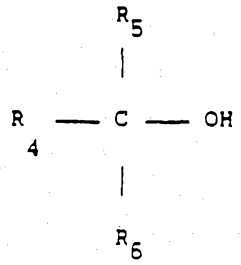
The molar ratio of hydroperoxide to alkane may also vary within wide limits; a minimum of 0.001 molar % is however recommended to enable an appreciable degree of conversion of the alkane to be observed; this ratio may be as high as 100 %. Preferably, this ratio is between 0.01 and 25 %.

The reaction may of course be conducted with a large excess of alkane which then also serves as diluent. It is also possible to operate in the presence of diluents or solvents that are not oxidisable in the conditions of the reaction, such as benzene and chlorobenzene.

According to an advantageous alternative of the present process, the reaction is conducted in the presence of a diluent selected among the saturated alcohols, the saturated diols and polyols, water and mixtures of

these.

The saturated alcohols that are suitable for carrying out the present process have the general formula (III) below:



(III)

in which:

- R_4 to R_6, which may be the same or different, represent:
  * hydrogen atoms,
  * linear or branched alkyl groupings having 1 to 30 carbon atoms,
  * cycloalkyl groupings having 3 to 12 carbon atoms,
  * alkyl- or cycloalkylaromatic groupings having 7 to 30 carbon atoms, or
  * aryl groupings, optionally substituted by one or two alkyl groupings containing up to 4 carbon atoms, aryl groupings having 6 to 20 carbon atoms;
- two of the R_4 to R_6 groupings together may moreover form a single divalent alkylene radical containing 4 to 10 carbon atoms,
- the three R_4 to R_6 groupings together may moreover form a single trivalent polycyclic radical containing 6 to 20 carbon atoms.

The saturated diols and polyols comprise a skeleton of general formula (III) above on which at least one supplementary hydroxyl group is introduced and, preferably, up to 6 supplementary hydroxyl groups.

As examples of such diluents one may mention: methanol, ethanol, isopropanol, tertiary butanol, 1-hexanol, 1-octanol, 1-dodecanol, cyclohexanol, dimethylphenylcarbinol, ethylene glycol, 1,3-propanediol and 2,4-dimethyl-2,4-dihydroxypentane.

The saturated alcohol used as diluent may of course be of the same nature as or of a different nature from the alcohol produced in the reaction; it is also possible to use as diluent a mixture containing an alcohol endogenous to the reaction medium and an alcohol exogenous to it.

It is preferred to use water or a saturated alcohol of formula (III) above in which R_1 to R_6, which may be the same or different, represent linear alkyl groupings having 1 to 4 carbon atoms or, a hydrogen atom.

Tertiary butanol is more particularly suitable for the performance of the process.

As indicated above it is possible to use mixtures of diluents and in particular a mixture of saturated alcohol (or saturated diol or polyol) and water. Good results are in particular obtained with a mixture of tertiary butanol and water.

The quantity of diluent or mixture of such diluents may vary within wide limits: an appreciable influence is observed when this quantity is of the order of 2 % by weight of alkane to be oxidised and no positive effect is observed when this quantity exceeds 200 % by weight of alkane. Good results are obtained for a quantity of diluent(s) between 2 and 100 % by weight of alkane.

When a mixture of alcohol and water is used, the quantity of water is not critical; it may vary within wide limits.

Depending on the precise water content of the reaction medium, the precise nature of the alcohol and/or the alkane the presence of a single phase or of two phases may be observed: an organic phase and an aqueous phase. The presence of such a two-phase system particularly at the end of reaction is another advantage linked to the process of the present invention to the extent that the products of oxidation and the unreacted alkane may be separated by decantation or extraction from the catalyst system the larger part of which is to be found in the aqueous phase at the end of the reaction. The residual aqueous phase may easily be used, if necessary after treatment, to catalyse a new oxidation reaction.

The Applicant has observed that it is also advantageous to operate in the presence of a buffer mixture so that the pH of the aqueous phase is maintained between 2 and 14. To this end it is particularly recommended that

one or more of the following compounds be added to the reaction medium: alkali metal hydroxides, inorganic or organic oxyacids and their alkali or alkaline earth metal salts and in particular, acetic acid and its salts, phosphoric acid and its salts, and boric acid and its salts.

The reaction temperature depends on the precise nature of the alkane to be oxidised and that of the organic hydroperoxide. It is generally between 50 and 180°C, and preferably between 70 and 150°C.

The reaction is performed at atmospheric pressure or if necessary at a pressure above atmospheric pressure so as to maintain the constituents of the reaction mixture in the liquid phase.

Reaction time (or residence time) generally between a few minutes and several hours may be adjusted, taking account of the objectives of production, the quantity of catalyst and the other reaction parameters.

At the end of the reaction the products may be recovered by any appropriate means, e.g. by distillation.

The following examples illustrate the invention.

The following conventions are used therein:

- DC designates: the degree of conversion of the organic hydroperoxide involved in the reaction.
- YD designates: the yield of a product (or mixture of products) in

relation to the converted hydroperoxide.

- YD (OLONE) : designates the yield of mixture of cyclohexanol and cyclohexanone.
- YD (OL) : designates the yield of cyclohexanol.
- YD (8-OL) : designates the yield of cyclooctanol.
- YD (8-ONE) : designates the yield of cyclooctanone.
- YD (8-OLONE) : designates the yield of mixture of cyclooctanol and cyclooctanone.
- YD (DMPC) : designates the yield of dimethylphenylcarbinol.
- YD (A+D) : designates the yield of mixture of acetophenone and dimethylphenylcarbinol.
- CHPO : designates cumyl hydroperoxide
- CHHPO : designates cyclohexyl hydroperoxide
- T : designates temperature

EXAMPLE 1:

In a 20 ml Carius type glass tube the following are charged at room temperature:

- OsO_4 (28 mg, 0.1 mmol) in solution in cyclohexane.

- cyclohexane deoxygenated with argon (5 ml, 46 mmol) and,

- cyclohexyl hydroperoxide (100 mg, 0.9 mmol).

A magnetic bar is added and the tube is purged with a current of argon. The tube is cooled with dry ice, and sealed. The whole is then heated to 100°C for 22 hours. The reaction mass is then analysed iodometrically and by gas phase chromatography.

99 % of the cyclohexyl hydroperoxide has been converted:

YD (OL) = 89 %

YD (ONE) = 46 %

YD (OLONE) = 135 %

EXAMPLE 2:

In a 1.9 ml glass phial, closed with a Teflon^{R}-coated cap the following are charged:

- Osmium as a 5 % deposit on charcoal (0.48 mg) (24 micrograms of osmium, i.e. $1.26.10^{-4}$ mmol of osmium)
- cyclooctane (0.82 g, 7.32 mmol)
- orthodichlorobenzene (10.5 mg) (standard for GPC)
- 99 % cumyl hydroperoxide (CHPO) (11.5 mg, 0.75 mmol)

The phial is immersed in an oil bath thermostated at 100°C for 17 hours, the reaction medium being stirred by a magnetic bar.

The degree of conversion of the CHPO is 100 % and the results obtained were as follows:

YD (8-OL) = 18 %

YD (8-OLONE) = 38 %

YD (DMPC) = 80 %

YD (A+D) = 84.5 %

EXAMPLE 3:

In a glass reactor of 200 ml capacity, equipped with a descending condenser, a gas inlet and outlet, a septum stopper, stirred by a magnetic bar and purged with argon, the following are introduced:

- cyclooctane (21 g, 187 mmol)
- tertiary butanol (8 g, 108 mmol)
- 1 M H_3BO_3/NaOH buffer (pH = 12.7) (2.5 ml)
- osmium in the form of triosmium dodecacarbonyl ($6.7.10^{-4}$ mmol) in solution in chlorobenzene (0.20 mg of solution).

The reaction medium is heated to 80°C then, cumyl hydroperoxide (CHPO) (0.79 g, 5.15 mmol) is injected through the septum stopper in the course of 20 seconds.

The degree of conversion of the CHPO is followed iodometrically; at the end of the test the reaction mass is homogenised by addition of tert-butanol and analysed by gas phase chromatography.

After 3.1 hours of reaction at temperature the results are as follows:

DC (CHPO) = 97 %

YD (8-OL) = 56.6 %

YD (8-ONE) = 8.1 %

YD (A + D) = 97.6 %

EXAMPLES 4 to 8:

In a glass tube and following an operating procedure which are analogous to those described in Example 1 a series of tests is carried out on a charge containing:

- cyclohexane (5.1 g, 60.7 mmol)
- 96 % cyclohexyl hydroperoxide (0.40 g, 3.3 mmol)
- tertiary butanol
- osmium tetroxide in solution in cyclohexane

The duration of each test is 24 h.

The particular conditions and the results obtained are shown in table I below:

TABLE I:

Ref	OsO_4/CHHPO mol/mol	t-BuOH* (%)	T °C	DC (%)	YD(OL) (%)	YD(OLONE) (%)
4	1.9.10-4	21	130	92.3	128.2	153.8
5	1.3.10-4	20	150	100	108.1	133.8
6	1.5.10-4	102	150	100	111.9	129.0
7	47.10-4	22	120	100	132.7	151.6
8	47.10-4	86	120	100	132.8	146.5

* t-BuOH: weight ratio of t-BuOH to cyclohexane.

EXAMPLES 9 and 10:

In a 1.9 ml glass phial, closed with a Teflon^{R}-coated cap, the following are charged:

- cyclohexane (1.10 g, 13.1 mmol)
- 96 % cyclohexyl hydroperoxide (0.0144 g, 0.124 mmol)
- osmium tetroxide ($1.01.10^{-4}$ mmol) in solution in cyclohexane
- dichlorobenzene (0.082 g) (standard for HPLC)
- in Example 9 only, tertiary butanol (0.047 g, 0.632 mmol).

The phial is immersed in an oil bath thermostatted at 120°C for 20 hours. The results and particular conditions are shown in Table II below. The degree of conversion of the CHHPO is 100 % in both cases.

TABLE II

Ref	OsO_4/CHPO mol/mol	t-BuOH	YD(OL) (%)	YD(OLONE) (%)
09	$8.14.10^{-4}$	NO	134	159
10	$8.14.10^{-4}$	YES	161	173

EXAMPLES 11 to 13:

In the reactor and according to the operating procedure which are analogous to those described for Example 3 a series of tests is carried out, it being stipulated that in the context of these tests the reaction mass is not homogenised at the end of the tests, on a charge containing:

- cyclooctane (30 g, 268 mmol)
- t-butanol (7.7 g, 104 mmol)
- deionized water (0.12 g, 6.7 mmol)
- osmium tetroxide in solution in cyclooctane the quantity of which is indicated in table (III) below:

The temperature having been raised to 80°C the following is injected in the course of 20 seconds:

99 % cumyl hydroperoxide (CHPO) (1.6 g, 10.4 mmol).

The results obtained at the end of 5 hours reaction are also shown in Table III below, the degree of conversion of CHPO being 100 % in all cases.

TABLE III:

Ref	OsO_4/CHPO mol/mol	YD(8-OL) (%)	YD(8-OLONE) (%)	YD(DMPC) (%)	YD(A+D) (%)
11	8.8.10-2	46	77	94	100
12	7.9.10-3	54	78	93	100
13	8.4.10-5	75	81.8	92	100

EXAMPLES 14 to 18:

In the reactor and according to the operating procedure analogous to those described for Example 3 a series of tests is carried out, it being stipulated that in the context of these tests the reaction mass is not homogenised at the end of the tests, on a charge containing:

- cyclooctane (30 g, 268 mmol)
- osmium tetroxide ($8.4.10^{-4}$ mmol) in solution in cyclohexane and if necessary:
- tert-butanol and
- deionized water.

The temperature having been raised to 80°C, cumyl hydroperoxide (1.6 g, 10.4 mmol) is injected in the course of 20 seconds. (The reaction medium is homogeneous).

The particular conditions and the results obtained are shown in table IV below, the degree of conversion of CHPO being 100 % in all cases.

TABLE IV:

Ref	t-BuOH(*) (% wt)	H_2O (*) (% wt)	Duration (h)	YD (8-OL) (%)	YD (8-OLONE) (%)	YD (DMPC) (%)	YD (A+D) (%)
14	0	0	< 1,5	26,3	46,8	88,2	92,2
15	2,7	0	< 1	40,4	55,1	89,3	94,2
16	2,8	0,043	1,5	45,4	59,1	91,2	95,9
17	25,4	0	4	72,0	79,7	92,8	100
13	26	0,4	5,0	75,0	81,8	91,9	100
18	100	0	5,0	76,8	82,7	85,7	100

* weight ratio relative to cyclooctane

EXAMPLE 19:

Example 17 above is reproduced replacing the t-butanol by an identical quantity of isopropanol.

The results obtained are as follows:

DC (CHPO) = 100 %

YD (8-OL) = 55.8 %

YD (8-OLONE) = 58.8 %

YD (DMPC) = 94.2 %

YD (A + D) = 100 %

EXAMPLE 20:

Example 17 above is reproduced replacing the t-butanol by an identical quantity of methanol.

The results obtained are as follows:

DC (CHPO) = 100 %

YD (8-DL) = 60 %

YD (8-OLONE) = 66 %

YD (DMPC) = 95 %

YD (A + D) = 99 %

EXAMPLE 21:

Following the operating procedure described in Examples 11 to 13 the following are charged:

- cumene (30 g, 250 mmol)
- osmium ($7.0.10^{-4}$ mmol) in the form of osmium tetroxide in solution in cyclohexane.

The temperature having been raised to 100°C, 99 % cumyl hydroperoxide (CHPO) (1.71 g, 11.2 mmol) is injected in the course of 20 seconds. After 2 h 30 min., the temperature is raised to 130°C. The mixture is analysed after the reaction has proceeded for 6 h 20 min. The results are as follows:

DC (CHPO) = 98 %

YD (DMPC) = 115 %

YD (A + D)= 165 %

EXAMPLE 22:

In a 1.9 ml glass phial, closed with a Teflon^{R}-coated cap, the following are charged:

- n-hexane (0.659 g, 7.65 mmol)
- 99 % cumyl hydroperoxide (0.0072 g, 0.047 mmol)
- osmium tetroxide ($7.72.10^{-5}$ mmol) in solution in cyclohexane

- orthodichlorobenzene (0.0074 g) (standard for GPC)
- tert-butanol (0.234 g, 3.15 mmol)

The phial is immersed in an oil bath thermostated at 120°C for 18 hours.

The results obtained are as follows:

YD (hexanal + 2-hexanone) = 1.5 %

YD (3-hexanone) = 1.1 %

YD (1-hexanol) = 1.8 %

YD (2-hexanol) = 29.5 %

YD (3-hexanol) = 25.3 %

YD (hexanol + hexanone) = 59.2 %

YD (DMPC) = 71 %

YD (A + D) = 100 %

EXAMPLES 23 to 26:

In a 1.9 ml glass phial, closed with a Teflon^{R}-coated cap, the following are charged:

- cyclohexane (0.755 g, 8.95 mmol)
- 99 % cumyl hydroperoxide (0.025 g, 0.163 mmol).
- osmium tetroxide ($3.8.10^{-5}$ mmol) in solution in cyclohexane.
- tert-butanol

(The medium is homogeneous).

The phial is immersed in an oil bath thermostated at 100°C for 40 hours.

The degree of conversion of CHPO is 100 %.

The particular conditions and the results obtained are shown in Table (V) below:

TABLE V:

Ref	t-BuOH(*) (% wt)	YD(OL) (%)	YD(OLONE) (%)	YD(DMPC) (%)	YD(A+D) (%)
23	0	70.2	84.5	91.4	97.1
24	3.3	84.5	94.1	95.0	100
25	23	92.5	97.9	90.8	100
26	63	88.3	93.0	81.5	100

* weight ratio relative to cyclohexane.

EXAMPLE 27:

In the phial and following the operating procedure described for Examples 23 to 26, a test was carried out on a charge consisting of:

- cyclooctane (0.800 g, 7.15 mmol)
- 99 % cumyl hydroperoxide (0.034 g, 0.226 mmol)
- osmium tetroxide ($1.9.10^{-5}$ mmol) in solution in cyclohexane.
- 2,4-dimethyl-2,4-dihydroxypentane (0.022 g, 0.166 mmol).

The degree of conversion of the CHPO is 100 %.

- YD (8-OL) = 47.7 %
- YD (8-OLONE) = 59.5 %
- YD (DMPC) = 86.1 %
- YD (A + D) = 92.2 %

EXAMPLE 28:

Example 27 above is reproduced with these differences, that a molar equivalent quantity of osmium trichloride in solution in tert-butanol is charged instead of the tetroxide, and tert-butanol (640 mg, 7.6 mmol) instead of the diol.

The degree of conversion of the CHPO is 100 %.

- YD (8-OL) = 68.6 %
- YD (8-OLONE) = 74.4 %
- YD (A + D) = 92.0 %

EXAMPLES 29 to 33:

In the reactor and following the operating procedure which are described for Example 3, a series of tests is carried out by injecting in each case 99 % cumyl hydroperoxide (0.79 g, 5.15 mmol) in the course of 20 seconds onto a charge containing:

- cyclooctane (21 g, 187 mmol)
- osmium tetroxide whose precise quantity is shown in Table VI below
- an aqueous phase (2.5 ml) and, if necessary,
- t-butanol (8.0 g, 108 mmol),

and maintained at 80°C.

Aqueous phase (PA1) comprises deionized water.

Aqueous phase (PA2) comprises a molar solution of the H_3BO_3/NaOH buffer in deionized water (pH = 12.7).

Aqueous phase (PA3) comprises a molar solution of the CH_3COOH/NaOH buffer in deionized water (pH = 5.3).

The particular conditions and the results obtained are collated in Table VI below:

TABLE VI:

Ref	OsO_4/CHPO mol/mol	t-BuOH	(*)	Duration (h)	DC(CHPO) (%)	YD(8-OL) (%)	YD(8-OLONE) (%)
29	$1.12.10^{-3}$	yes	PA1	0.5	98	64.7	66.7
30	$1.10.10^{-4}$	yes	PA1	7.0	33	nd	nd
31	$1.10.10^{-4}$	yes	PA2	3.0	97	59.5	67.7
32	$1.10.10^{-4}$	no	PA2	5.2	99.7	20.4	28.1
33	$1.60.10^{-3}$	yes	PA3	8.0	98.3	82.7	86.1

(*): nature of the aqueous phase used

nd : not determined

EXAMPLE 34:

In a glass reactor equipped with a condenser, a magnetic bar stirrer and an overflow to limit the reaction mass to 72 ml, the following are introduced:

Cyclohexylhydroperoxide, 96%	:	0.351 g (2.9 m.mol)
Cyclohexanone	:	0.482 g (4.91 m.mol)
Cyclohexanol	:	3.194 g (31.9 m.mol)
Cyclohexane	:	54 g
OsO_4 in cyclohexane solution	:	0.0112g (0.044 m.mol)

The reaction mixture is stirred and heated under reflux (81°C). After ten minutes, the mass has a black colour. The following are injected simultaneously via Teflon tubes:

OsO_4 in cyclohexane solution at 1.00 m.mol/l: 6.91g/h (8.9 micromol/h)

Cyclohexylhydroperoxide in cyclohexane solution at 6% by wt: 414 m.mol/l:117g/h (60.7 m.mol/h)

The reflux is maintained by heating.

After two hours of operation, a steady state is reached. The flow leaving via the overflow is then collected and analysed.

Molar ratio CHHPO introduced/osmium introduced: 6974

Reaction time : 26.5 minutes

DC (CHHPO): 99.2% (Residual CHHPO/cyclohexane = 3.5×10^{-4})

Activity of the osmium: 4.3 catalytic cycles per second

YD (6-ONE) : 30%

YD (6-OL) : 105.5%

YD (6-OLONE) : 135.5%

The Claims defining the invention are as follows:

1. Process for the oxidation of an alkane with an organic hydroperoxide to produce a mixture of alcohols and ketones, which comprises contacting a said alkane and a said hydroperoxide at a temperature above 20°C in the presence of a catalytic quantity of osmium or an osmium compound.

2. Process according to claim 1, in which the alkane used has the formula:

RH (I)

in which R represents a linear or branched alkyl group having 1 to 30 carbon atoms; a cycloalkyl group having 3 to 12 carbon atoms in the ring, and unsubstituted or substituted by one or more alkyl groups of up to 4 carbon atoms each; a polycycloalkyl group having 2 to 5 rings each of which may contain 3 to 12 carbon atoms; or an alkyl- or cycloalkyl-aromatic group having 7 to 30 carbon atoms.

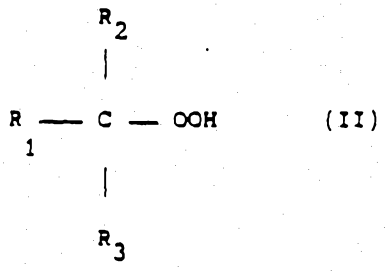
3. Process according to claim 2, in which the alkane is of formula (I) in which R represents:

- a linear or branched alkyl group of 1 to 12 carbon atoms,
- a cycloalkyl group of 5 to 12 carbon atoms in the ring,
- an alkylbenzene residue in which the alkyl group contains up to 4 carbon atoms, or
- a cycloalkylbenzene residue in which the

cycloalkyl group contains 5 to 8 carbon atoms.

4. Process according to claim 1, in which the alkane used is cyclohexane.

5. Process according to any one of claims 1 to 4, in which the organic hydroperoxide used has the formula:



(II)

in which R_1, R_2 and R_3, which may be the same or different, each represent hydrogen, a linear or branched alkyl group of 1 to 30 carbon atoms, a cycloalkyl group of 3 to 12 carbon atoms, an alkyl- or cycloalkyl-aromatic group of 7 to 30 carbon atoms, or

an aryl group, unsubstituted or substituted by one or two alkyl groups of up to 4 carbon atoms each or aryl groups having 6 to 20 carbon atoms each; and

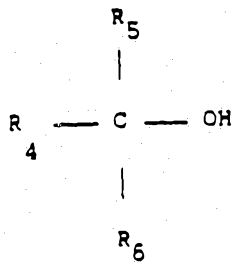
two of the groups R_1, R_2 and R_3 may together form a single divalent alkylene radical of 4 to 10 carbon atoms.

6. Process according to claim 5, in which the organic hydroperoxide of formula (II) in which R_1, R_2 and R_3, which may be the same or different, each represent hydrogen, alkyl of 1 to 4 carbon atoms, or phenyl, and two of them together may represent a divalent radical forming with the carbon atom to which it is attached a cyclohexyl or cyclooctyl residue, not more than one of R_1, R_2 and R_3 being hydrogen.

7. Process according to any one of claims 1 to 4 in which the hydroperoxide used is cyclohexyl hydroperoxide.

8. Process according to any one of the preceding claims, in which the oxidation is carried out in the presence of a diluent which is a saturated alcohol, a saturated diol or polyol, water or a mixture thereof.

9. Process according to claim 8, in which the process is carried out in the presence of an alcohol of formula:



(III)

in which:

- R_4, R_5 and R_6, which may be the same or different, each represent:

hydrogen, a linear or branched alkyl group of 1 to 30 carbon atoms, a cycloalkyl group of 3 to 12 carbon atoms, an alkyl- or cycloalkyl- aromatic group of 7 to 30 carbon atoms, or an aryl group, unsubstituted or substituted by one or two substituent alkyl groups of up to 4 carbon atoms each, or aryl groups having 6 to 20 carbon atoms each; and

- two of the groups R_4, R_5 and R_6 may together form a single divalent alkylene radical of 4 to 10 carbon atoms, and R_4, R_5 and R_6 may together form a single trivalent polycyclic radical containing 6 to 20 carbon atoms.

10. Process according to claim 9, in which the alcohol has the formula (III) in which R_4, R_5 and R_6, which may be the same or different, each represent linear alkyl groups of 1 to 4 carbon atoms each or hydrogen.

11. Process according to claim 9, in which the alcohol used is tert-butanol.

12. Process according to any one of claims 8 to 11, in which the alcohol represents 2 to 200% and preferably 2 to 100% relative to the weight of the alkane.

13. Process according to any one of claims 8 to 12, in which the process is carried out in the presence of a mixture of alcohol and water.

14. Process according to any one of the preceding claims, in which the quantity of osmium used is between 10^{-2} and 10^{-5} mole per mole of the hydroperoxide.

15. Process according to any one of the preceding claims, in which the organic hydroperoxide represents from 0.001 to 100% (molar) of the alkane, and preferably from 0.01 to 25% (molar).

16. Process according to any one of the preceding claims, in which the reaction temperature is between 70 and 150°C.

17. Process according to any one of the preceding claims, in which the osmium is introduced in the form of metallic osmium, if necessary deposited on a support, in the form of an inorganic compound of osmium, or in the form of an organic complex of osmium which releases an inorganic form of osmium in the reaction medium.

18. Process according to claim 17, in which the osmium is introduced in the form of osmium tetroxide.

19. Process according to any one of the preceding claims, in which the reaction is conducted in the liquid phase.

20. Process according to claim 1, substantially as described in any one of the foregoing Examples.

21. Mixtures of alcohols and ketones when produced by the process of any of claims 1 to 20.

22. The steps, features, compositions and compounds disclosed herein or referred to or indicated in the specification and/or claims of this application, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this SECOND day of MARCH 1989

Rhone-Poulenc Chimie

by DAVIES & COLLISON
Patent Attorneys for the applicant(s)