

The subject of the present invention is a process for the catalytic oxidation of alkanes to mixtures of alcohols and ketones.

5 The catalytic oxidation of alkanes by organic hydroperoxides is a reaction known in itself and various catalytic systems have already been proposed for conducting this reaction.

Thus, D. Mansuy et al. in Angew. Chem. Int. Eng. Ed. 19 (1980) n° 11, pages 909-910 described the
10 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
15 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
20 greatly impaired.

Moreover French Patent Application n° 2 559 154 describes in particular the oxidising deperoxidation of t-butyl and cumyl hydroperoxides in cyclohexane or octane in which the catalyst is a cobalt complex carrying in
25 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
30 very poor efficiency. That Application evokes 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
35 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 subject of the present invention is hence a process for the oxidation of alkanes to a mixture of alcohols and ketones with an organic hydroperoxide in the presence of an osmium-based catalyst, characterised in that 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 into the reaction medium, and in that the process is carried out at a temperature of between 50 and 180°C.

By alkanes, substrates in the context of the present process, there are understood saturated hydrocarbons corresponding to formula (I) below:



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,
- a polycycloalkyl group comprising from 2 to 5 rings each of which may contain 3 to 12 carbon atoms, or
- an alkyl- or cycloalkylaromatic group having 7 to 30 carbon atoms.

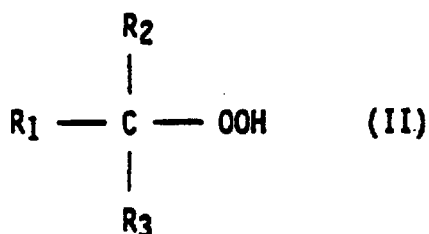
More specifically R represents:

- 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.

As examples of oxidisable alkanes in the context of the present process one may mention methane, ethane, propane, isobutane, isopentane, butane, hexane, octane, cyclopentane, cumene, toluene, tetralin, decalin, cyclododecane and pinane.

In the context of the present process use is also made of an organic hydroperoxide. This compound may be represented by general formula (II) below:



in which:

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

- * hydrogen atoms,
 - * linear or branched alkyl groups having 1 to 30 carbon atoms,
 - * cycloalkyl groups having 3 to 12 carbon atoms,
 - * alkyl- or cycloalkylaromatic groups having 7 to 30 carbon atoms, or
 - * aryl groups, optionally substituted by one or two alkyl groups containing up to 4 carbon atoms, aryl groups having 6 to 20 carbon atoms;
- two of the R_1 to R_3 groups together may moreover form a single divalent alkylene radical containing 4 to 10 carbon atoms.

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

- alkyl groups having 1 to 4 carbon atoms

- phenyl groups, or
- for two of them a single divalent radical forming with the carbon atom to which it is attached a cyclohexyl or cyclooctyl residue, or
- 5 - for one of them, 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.

10 As indicated at the beginning of the present specification, in the context of the present process a mixture is obtained 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
15 substrate. Thus from cyclohexane a mixture of cyclohexanol and cyclohexanone will be obtained, which are useful intermediates in various manufacturing processes (adipic acid, caprolactam), a mixture commonly referred to as OLONE. In the same way starting from
20 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.

25 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
30 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 ex-
35 amples of such compounds one may mention: OsO , Os_2O_3 , OsO_2 , OsO_4 , OsCl_3 , K_2OsO_4 , NaOsF_6 , OsOCl_4 , $\text{K}_2\text{OsO}_4(\text{OH})_2$, 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
5 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
10 one of the following group:

Os/C, Os₃(CO)₁₂, OsO, Os₂O₃, OsO₂, OsO₄ and OsCl₃.

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

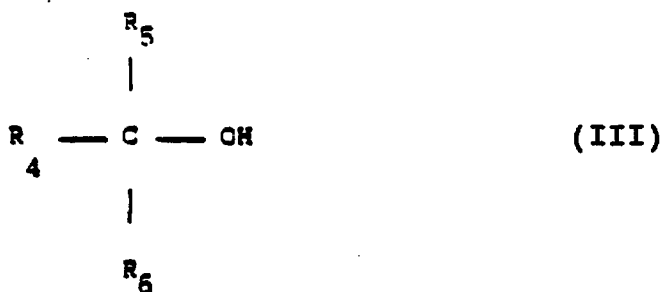
The quantity of osmium to be involved is not
15 critical and may vary within wide limits. For good performance of the invention it will be at least 10⁻⁶ mole of osmium per mole of hydroperoxide and there is no observable advantage in exceeding a quantity of 10⁻¹ mole of osmium per mole of hydroperoxide. This quantity is,
20 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 0.1 molar % is however recommended to enable an appreciable degree of
25 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.
30 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
35 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:



5 in which:

- R_4 to R_6 , which may be the same or different, represent:

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

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

20 EXAMPLE 1:

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

- OsO₄ (28 mg, 0.1 mmol) in solution in cyclohexane.
- 25 - 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
30 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:

35	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:

- 5 - 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)
- ortho-dichlorobenzene (10.5 mg) (standard for GPC)
- 10 - 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.

15 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 %
20 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:

- 25 - cyclooctane (21 g, 187 mmol)
- tertiary butanol (8 g, 108 mmol)
- 1M H₃BO₃/NaOH buffer (pH = 12.7) (2.5 ml)
- osmium in the form of triosmium dodecacarbonyl
30 (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.

35 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 %
5	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
 - 15 - 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:

20	Ref	OsO ₄ /CHHPO mol/mol	t-BuOH* (%)	T °C	DC (%)	YD(OL) (%)	YD(OLONE) (%)
	4	1,9.10x4	21	130	92,3	128,2	153,8
	5	1,3.10x4	20	150	100	108,1	133,8
	6	1,5.10x4	102	150	100	111,9	129.0
	7	47.10x4	22	120	100	132,7	151.6
	8	47.10x4	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)
- deionised 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 II [sic] 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	8.8.10x2	46	77	94	100
12	7.9.10x3	54	78	93	100
13	8.4.10x5	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
- deionised 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 ₂ O (*) (% wt)	Duration (h)	YD (8-OL) (%)	YD (8-OLONE) (%)	YD (DMPC) (%)	YD (A+D) (%)
14	0	0	1.5	25.3	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

5 * 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:

10 DC (CHPO) = 100 %
 YD (8-OL) = 55.8 %
 YD (8-OLONE) = 58.8 %
 YD (DMPC) = 94.2 %
 YD (A + D) = 100 %

15 **EXAMPLE 20:**

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

The results obtained are as follows:

20 DC (CHPO) = 100 %
 YD (8-OL) = 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)
- 5 - 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
10 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 %
15	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)
- 20 - 99% cumyl hydroperoxide (0.0072 g, 0.047 mmol)
- osmium tetroxide (7.72×10^{-5} mmol) in solution cyclohexane
- ortho-dichlorobenzene (0.0074 g) (standard for GPC)
- 25 - 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 %
30	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 %
35	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 (*)	YD(OL)	YD(OLONE)	YD(DMPC)	YD(A+D)
	(% wt)	(%)	(%)	(%)	(%)
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 %

5 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,
10 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 %

15 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
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,
- 25 - t-butanol (8.0 g, 108 mmol), and maintained at 80°C.

Aqueous phase (PA1) comprises deionised water.

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

30 Aqueous phase (PA3) comprises a molar solution of $CHF_3CH_2COOH/NaOH$ buffer in deionised 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 ⁻⁴	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

The following are introduced into a glass reactor equipped with a condenser, a magnetic bar and a weir limiting the reaction mass to 72 ml:

- 96% cyclohexyl hydroperoxide : 0.351 g (2.9 mmol)
- cyclohexamone : 0.482 g (4.91 mmol)
- cyclohexanol : 3.194 g (31.9 mmol)
- cyclohexane : 54 g
- OsO₄ in cyclohexane solution : 0.0112 g (0.044 mmol)

The reaction mixture is stirred and heated to reflux (81°C).

After 10 minutes the mass is black in colour.

The following are then injected simultaneously via teflon tubing:

- OsO₄ in cyclohexane solution at a concentration of 1.00 mmol/l : 6.91 g/h (8.9 micromol/h)
- Cyclohexyl hydroperoxide in cyclohexane solution at a concentration of 6 % by weight : 414 mmol/l : 117 g/h (60.7 mmol/h)
- Reflux is maintained by heating.

After two hours' operation a steady state is reached; the stream leaving via the weir is then

collected and analysed.

Molar ratio HPOCH introduced/osmium introduced : 6974

Residence time : 26.5 minutes

DC (HPOCH) : 99.2 % (residual {HPOCH}/{cyclohexane} =

5 3.5×10^{-4})

Osmium activity : 4.3 catalysis cycles/second

YD (6-ONE) : 30 %

YD (6-OL) : 105.5 %

YD (6-OLONE) : 135.5 %



CLAIMS

1. Process for the catalytic oxidation of compounds of the general formula



(I)

5 in which R represents:

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

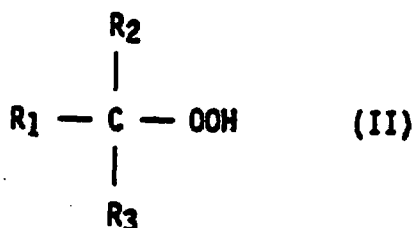
- a cycloalkyl group having 3 to 12 carbon atoms in the ring, optionally substituted by one or more alkyl groups containing up to 4 carbon atoms,

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

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

15 to a mixture of alcohols and ketones with an organic hydroperoxide in the presence of an osmium-based catalyst, characterised in that 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
20 or in the form of an organic complex of osmium which releases an inorganic form of osmium into the reaction medium, and in that the process is carried out at a temperature of between 50 and 180°C.

2. Process according to Claim 1, characterised in that
25 the organic hydroperoxide has the general formula:



in which:

- R₁ to R₃, which may be the same or different, represent:

* hydrogen atoms,

* linear or branched alkyl groups having 1 to 30 carbon atoms,

* cycloalkyl groups having 3 to 12 carbon atoms,

* alkyl- or cycloalkylaromatic groups having 7 to 30 carbon atoms, or



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

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

3. Process according to any one of the preceding claims, characterised in that the compounds of formula (I) given in Claim 1 are selected from among those for which R represents:

- 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.

4. Process according to any one of the preceding claims, characterised in that the organic hydroperoxide has the formula (II) given in Claim 2 in which R_1 to R_3 , which may be the same or different, represent:

- alkyl groups having 1 to 4 carbon atoms

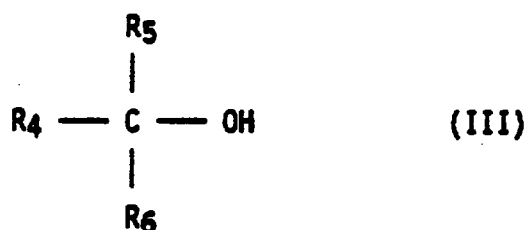
- phenyl groups, or

- for two of them a single divalent radical forming with the carbon atom to which it is attached a cyclohexyl or cyclooctyl residue, or

- for one of them, a hydrogen atom.

5. Process according to any one of the preceding claims, characterised in that the process is carried out in the presence of a diluent selected among the saturated alcohols, the saturated diols and polyols, water and mixtures of these.

6. Process according to Claim 5, characterised in that the process is carried out in the presence of an alcohol of formula



in which:

- R_4 to R_6 , which may be identical or different, represent:

- * hydrogen atoms,
- 5 * linear or branched alkyl groups having 1 to 30 carbon atoms,
- * cycloalkyl groups having 3 to 12 carbon atoms,
- * alkyl- or cycloalkylaromatic groups having 7 to 30 carbon atoms, or
- 10 * aryl groups, optionally substituted by one or two alkyl groups containing up to 4 carbon atoms, aryl groups having 6 to 20 carbon atoms;
- two of the R_4 to R_6 groups together may moreover form a single divalent alkylene radical containing 4 to 10
- 15 carbon atoms,
- the three R_4 to R_6 groups together may moreover form a single trivalent polycyclic radical containing 6 to 20 carbon atoms.
- 7. Process according to Claim 6, characterised in that
- 20 the alcohol has the formula (III) in which R_4 to R_6 , which may be identical or different, represent linear alkyl groups having 1 to 4 carbon atoms or a hydrogen atom.
- 8. Process according to any one of Claims 5 to 7, characterised in that the alcohol represents 2 to 200 %
- 25 and preferably 2 to 100 % relative to the weight of the compound of formula (I) given in Claim 1.
- 9. Process according to any one of Claims 5 to 8, characterised in that the process is carried out in the presence of a mixture of alcohol and water.
- 30 10. Process according to any one of Claims 5 to 9, characterised in that the alcohol used is tert-butanol.



11. Process according to any one of the preceding claims, characterised in that the quantity of osmium is between 10^{-2} and 10^{-5} mole per mole of hydroperoxide.
- 5 12. Process according to any one of the preceding claims, characterised in that the organic hydroperoxide represents from 0.001 to 100 % (molar) of the compound of formula (I) given in Claim 1, and preferably from 0.01 to 25 % (molar).
- 10 13. Process according to any one of the preceding claims, characterised in that the reaction temperature is between 70 and 150°C.
14. Process according to any one of the preceding claims, characterised in that the osmium is introduced in the form of its tetroxide.
- 15 15. Process according to any one of the preceding claims, characterised in that the compound of formula (I) given in Claim 1 which is used is cyclohexane.
16. Process according to any one of the preceding claims, characterised in that the hydroperoxide used is
- 20 cyclohexyl hydroperoxide.
17. Process according to any one of the preceding claims, characterised in that the reaction is conducted in the liquid phase.