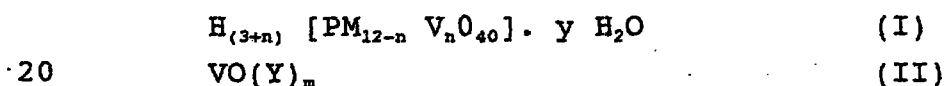


The present invention relates to a process for the preparation of aliphatic carboxylic acids by oxidation of cyclic ketones by means of molecular oxygen or of a gas in which it is contained.

5 Patent GB-A-999229 describes a process for the oxidation of compounds such as cyclohexanone, cyclohexyl hydroperoxide or 1,2-cyclohexanedione using an at least stoichiometric amount of a pentavalent vanadium compound. This vanadium compound is thus converted to a tetravalent
10 vanadium compound, which is itself reoxidized by nitric acid to the pentavalent compound.

More specifically, the subject of the present invention is a process for the preparation of aliphatic carboxylic acids by oxidation of monocyclic ketones by
15 means of molecular oxygen or of a gas in which it is contained, characterized in that the catalyst is chosen from the vanadium compounds corresponding to either of the formulae (I) and (II) below:



in which:

- n is an integer greater than or equal to 1 and less than or equal to 6,
- M represents a molybdenum or tungsten atom,
- 25 - y is an integer, which may be zero, and is less than 50,
- Y represents an acetylacetonate group or an alkoxy group containing 1 to 10 atoms,
- m has the value 2 or 3.

30 Monocyclic ketones, the starting materials, are understood, in the context of the present process, to refer to compounds in which the carbonyl group is directly bonded to carbon atoms in order to form a single saturated ring of 5 to 8 carbon atoms, it being
35 additionally possible for the ring to contain one or two substituents chosen from C₁-C₄ alkyl radicals and the phenyl group.

By way of examples of such ketones, there may be mentioned:

- cyclopentanone,
- cyclohexanone,
- 2-methylcyclohexanone,
- 2-methylcyclopentanone,
- 5 - 2,5-dimethylcyclopentanone
- 2,6-dimethylcyclohexanone and
- 2-phenylcyclohexanone.

Aliphatic carboxylic acids are understood to refer to keto acids and diacids. These acids are capable of being at least partially converted, in situ in the presence of an alcohol or an ether, to the corresponding esters or diesters, as soon as they are formed. The preparation of these partially or totally esterified forms of the acids in question enters into the context of the present process.

Cyclohexanone is a particularly preferred starting material, because it leads to adipic acid.

The process according to the present invention requires the use of a catalyst chosen from the vanadium compounds corresponding to either of the formulae (I) and (II) defined above.

By way of examples of vanadium compounds corresponding to the formula (I), there may be mentioned:

- 25 $H_4[PW_{11}V_1O_{40}] \cdot 30 H_2O$
- $H_4[PMo_{11}V_1O_{40}] \cdot 33 H_2O$
- $H_5[PMo_{10}V_2O_{40}] \cdot 30-36 H_2O$
- $H_6[PMo_9V_3O_{40}] \cdot 34 H_2O$

By way of examples of vanadium compounds corresponding to the formula (II), there may be mentioned:

- 30 - vanadyl bis(acetylacetonate) and
- isopropyl vanadate.

Within the context of the present process, it is preferred to make use of vanadium compounds corresponding to the formula (I) above.

More specifically, use is made of compounds corresponding to the formula (I) in which:

- n equals 1 or 2 and
- y is greater than or equal to 30 and less than or equal to 40.

An advantageous class of vanadium-based catalysts is formed by the compounds corresponding to the formula (I) indicated at the head of the present specification, in which M is a molybdenum atom.

5 These compounds (molybdo- or tungstovanadophosphoric acids) and their modes of preparation are known to a person skilled in the art. A reference may usefully be made to the article of Messrs. G. A. Tsigdinos and C. J. Hallada published in *Inorganic Chemistry*, Vol. 7, 10 March 1968, pages 437 and onwards, to that of P. Courtin, published in *Rev. Chim. Min.*, 1971, 8, 75 and to that of M. Canneri, in *Gazz. Chim. Ital.*, 1926, 56, 871.

 The amount of catalyst to be used may vary within a wide range. This amount, expressed in moles of vanadium 15 per litre of reaction medium, is generally between 0.001 and 0.5 mol.l⁻¹. This concentration is preferably between 0.005 and 0.1 mol.l⁻¹.

 The oxidation generally takes place in a liquid medium, the liquid medium comprising the monocyclic 20 ketone to be oxidized and, where appropriate, a solvent or diluent which is inert under the reaction conditions, with respect to the constituents of the reaction mixture.

 By way of examples of such solvents or diluents, there may be mentioned aromatic hydrocarbons which are 25 halogenated or otherwise, nitrohydrocarbons such as nitrobenzene and nitromethane, nitriles such as acetonitrile and carboxylic acids such as acetic acid, and water.

 The oxidation may also be carried out in a liquid 30 medium, the said medium comprising an alcohol and, in particular, a C₁-C₄ alkanol which is capable of reacting with the acid (or the diacid) produced in order to form the corresponding ester (or diester).

 Of course, the reaction medium may contain a 35 solvent mixture and, in particular, a mixture of a solvent which is inert in the sense indicated above and of an alcohol.

 The reaction medium may also contain an ether such as diglyme.

The initial concentration of the substrate to be oxidized may vary within a wide range. It is generally between 50 and 400 g.l⁻¹, preferably between 150 and 250 g/l⁻¹.

5 The temperature at which the process according to the present invention is carried out is usually between 25 and 120°C and is preferably between 40 and 100°C.

 Molecular oxygen, used as oxidizing agent in the present process, may be in the form of pure oxygen or of
10 mixtures of oxygen with other inert gases. It is thus possible to use air or alternatively oxygen/nitrogen mixtures which are richer or less rich in oxygen than air.

 The oxidation may be carried out under a stream
15 of oxygen or of gas containing oxygen or by charging a certain amount of oxygen. The oxygen partial pressure may range between 0.2 bar and 20 bar; in practice, however, it is not necessary for it to exceed 10 bar.

 At the end of the reaction or of the desired
20 reaction time, the products obtained may be recovered and separated by any appropriate means, for example by distillation.

 The examples below illustrate the present invention.

25 - EXAMPLES 1 TO 5:

 These examples illustrate the oxidation of 2-methylcyclohexanone.

 12.4 mmol of 2-methylcyclohexanone, the catalyst whose nature and the amount of which are indicated in the
30 table below, for Examples 2 to 5, and 6 cm³ of acetonitrile are placed in a 20 ml glass tube connected to a gasometer containing molecular oxygen.

 After the tube is closed, it is brought to 60°C with stirring for the period indicated in the table.

35 At the end of 4 hours (or 24 hours) at this temperature, the mixture is cooled and analysed by gas chromatography.

 The specific conditions and the results obtained

are featured in Table (I) below in which:

- S (OHA) denotes the selectivity towards 6-oxoheptanoic acid,

$$- \left[\frac{\text{number of moles of product formed}}{\text{number of moles of substrate converted}} \times 100 \right]$$

5 - DC denotes the degree of conversion of the 2-methylcyclohexanone.

TABLE I

Ex. No.	CATALYST		Time	DC	S(OHA)
	NATURE	mol.l ⁻¹	(h)	(%)	(%)
	VO(acac) ₂	0.12	24	49	89.0
	VO[OCH(CH ₃) ₂] ₃	0.02	24	57.5	89.5
	H ₄ [PW ₁₁ V ₁ O ₄₀]. 30 H ₂ O	0.02	4	57	89.5
	H ₄ [PMo ₁₁ V ₁ O ₄₀]. 33 H ₂ O	0.02	4	93.5	89.5
	H ₅ (PMo ₁₀ V ₂ O ₄₀]. 30-36 H ₂ O	0.01	4	98	89.0

- EXAMPLE 6:

10 This example illustrates the oxidation of cyclohexanone.

The procedure is performed in an analogous manner to Example 5 above, replacing 2-methylcyclohexanone by the same molar amount of cyclohexanone.

15 All other conditions being equal, adipic acid was obtained with a selectivity of 75 %, the degree of conversion of cyclohexanone being 85 %.

- EXAMPLE 7:

20 Example 5 above is repeated, replacing acetonitrile by the same volume of nitromethane. All other conditions being equal, the following results were obtained:

The degree of conversion of 2-methylcyclohexane: (DC) is 98 %.

The yield of 6-oxoheptanoic acid [RY (OHA)] is 81.5 %

$$\left[RY = \frac{\text{number of moles of product formed}}{\text{initial number of moles of substrate}} \times 100 \right]$$

- EXAMPLE 8:

5 Example 5 above is repeated, replacing acetonitrile by the same volume of acetic acid.

In 6 hours of reaction, all other conditions being equal, the following results were obtained:

DC = 81 %

10 RY (OHA) = 69 %

- EXAMPLE 9:

Example 5 above is repeated, replacing acetonitrile by the same volume of methanol.

15 In 6 hours of reaction, all other conditions being equal, the following results were obtained:

DC = 54 %

The yield of 6-oxoheptanoic acid methyl ester is 49 % [RY(EST)].

- EXAMPLE 10:

20 Example 5 above is repeated, replacing acetonitrile by the same volume of diglyme (CH₃-O-CH₂-CH₂-O-CH₃).

In 24 hours of reaction, all other conditions being equal, the following results were obtained:

25 DC = 96 %

RY(OHA) = 74 %

RY(EST) = 16 %

- EXAMPLE 11

30 Example 5 above is repeated, replacing 1 cm³ of acetonitrile by 1 cm³ of methanol.

In 6 hours of reaction, all other conditions

being equal, the following results were obtained:

DC = 96 %
 RY(OHA) = 4 %
 RY(EST) = 86 %

5 - EXAMPLES 12 to 14:

A series of tests are performed according to the experimental procedure described for Examples 1 to 5 above on a charge containing no solvent but 12.4 mmol (1.5 cm³) of 2-methylcyclohexanone, a catalyst whose nature and the amount of which are featured in Table (II) below, at 60°C under an oxygen partial pressure of one atmosphere. The specific conditions and the results obtained are featured in Table (II) below, in which the conventions used are as follows:

- 15 - DC denotes the degree of conversion of 2-methylcyclohexanone.
 - RY (OHA) denotes the yield of 6-oxoheptanoic acid

$$\left[\text{RY} = \frac{\text{number of moles of product formed}}{\text{initial number of moles of substrate}} \times 100 \right]$$

20

TABLE II

Ex. No.	CATALYST		TIME (h)	DC (%)	DC (OHA) (%)
	NATURE	mmol			
12	H ₅ [PMo ₁₀ V ₂ O ₄₀] · 30-36H ₂ O	0.075	8	90	75
13	VO[OCH(CH ₃) ₂] ₃	0.375	24	50	40
14	[VO(acac) ₂]	0.90	24	49	41

25 - EXAMPLE 15:

A test is performed, according to the experimental procedure described above, on a charge containing:

- 4.85 mmol of cyclohexanone
- 5 cm³ of acetonitrile

- 1 cm³ of methanol
- 0.05 mmol of H₅[PMo₁₀V₂O₄₀]. 30-36H₂O

The oxygen partial pressure is 1 atm. In 24 hours of reaction at 60°C the following results were obtained:

5

DC = 98 %

Yield of dimethyl adipate : 54 %.

- EXAMPLE 16 to 20:

10 A series of tests are performed according to the experimental procedure described above, starting from various substrates, under the following common conditions:

- H₅[PMo₁₀V₂O₄₀]. 30-36H₂O is used as catalyst
- the solvent is acetonitrile (6 cm³ except where otherwise indicated)
- 15 - the temperature is 60°C and
- the oxygen partial pressure is 1 atm.

The specific conditions and the results obtained are featured in Table III below, in which the following conventions are used:

20

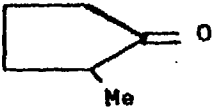
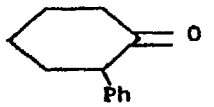
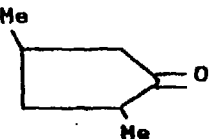
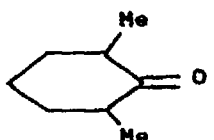
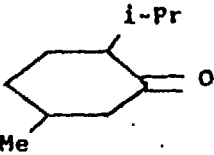
- DC is the degree of conversion of the ketone considered
- RY is the yield of the product considered

$$\left[RY = \frac{\text{number of moles of product formed}}{\text{initial number of moles of substrate}} \times 100 \right]$$

25

- Me represents a methyl radical
- Ph represents a phenyl radical
- i-Pr represents an isopropyl radical
- A the amount of catalyst charged

TABLE III

EX. No.	SUBSTRATE					PRODUCT	
	NATURE	mmol	A (mmol)	TIME h	DC (%)	NATURE	RY (%)
16		4.4	0.025	2	96	$\text{CH}_3\text{-C(O)-}(\text{CH}_2)_3\text{-COOH}$	94
17		2.4	0.015	6	96	$\text{Ph-C(O)-}(\text{CH}_2)_4\text{-COOH}$	90
18 (*)		4.0	0.025	2	99	$\text{CH}_3\text{-C(O)-CH}_2\text{-CH(CH}_3\text{)-CH}_2\text{-COOH}$	94
19		11.0	0.075	6	91	$\text{CH}_3\text{-C(O)-}(\text{CH}_2)_3\text{-CH(CH}_3\text{)-COOH}$	89
20		8.70	0.070	24	88	$\text{i-Pr-C(O)-}(\text{CH}_2)_2\text{-CH(CH}_3\text{)-CH}_2\text{-COOH}$	84

(*) 2 cm³ of acetonitrile



CLAIMS

1. Process for the preparation of aliphatic carboxylic acids chosen from aliphatic diacids and keto acids, by oxidation of monocyclic ketones chosen from compounds in which the carbonyl group is directly linked to carbon atoms to form single saturated ring containing 5 to 8 carbon atoms, the ring being able in addition to include one or two substituents chosen from C₁-C₄ alkyl radicals and the phenyl group, by means of molecular oxygen or of a gas in which it is contained, characterized in that the catalyst is chosen from the vanadium compounds corresponding to either of the formulae (I) and (II) below:



in which:

- n is an integer greater than or equal to 1 and less than or equal to 6,
- M represents a molybdenum or tungsten atom,
- y is an integer, which may be zero, and is less than 50,
- Y represents an acetylacetonate group or an alkoxy group containing 1 to 10 atoms,
- m has the value 2 or 3,

and in that the reaction is carried out in a liquid medium.

2. Process according to claim 1, characterized in that the liquid medium comprises a solvent or diluent which is inert under the reaction conditions with respect to constituents of the reaction mixture.

3. Process according to claim 1 or 2, characterized in that the solvent or diluent used is acetonitrile.

4. Process according to any one of the preceding claims, characterized in that the catalyst corresponds to the formula (I) given in claim 1.

5. Process according to claim 4, characterized in that the catalyst corresponds to the formula (I) in which n equals 1 or 2 and y is an integer greater than or equal



to 30 and less than or equal to 40.

6. Process according to claim 4 or 5, characterized in that catalyst corresponds to the formula (I) in which M represents a molybdenum atom.

5 7. Process according to any one of the preceding claims, characterized in that the temperature is between 25 and 120°C, and preferably between 40 and 100°C.

8. Process according to any one of the preceding claims, characterized in that the oxygen partial pressure
10 is between 0.2 and 20 bar.

9. Process according to any one of the preceding claims, characterized in that the vanadium concentration in the reaction medium is between 0.001 and 0.5 mol.l⁻¹, and preferably, between 0.005 and 0.1 mol.l⁻¹.

15 10. Process according to any one of the preceding claims, characterized in that the monocyclic ketone is cyclohexanone.

11. Process according to any one of the preceding claims, characterized in that the reaction medium con-
20 tains an alcohol.