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(54) Title: PROCESS FOR THE OXIDATION OF ORGANIC SUBSTRATES BY MEANS OF SINGLET OXYGEN AT HIGH REACTION TEMPERATURES

(57) Abstract: Process for the oxidation of organic substrates by means of singlet oxygen, in which organic substrates which react with ¹O₂ are admixed with 10-70% strength H₂O₂ in an organic solvent in the presence of a molybdenum-based catalyst at a pH of 9 - 14 and a temperature in the range from 50°C to the reflux temperature, whereupon the oxidation to the corresponding oxidation products occurs subsequent to the catalytic decomposition of H₂O₂ into water and ¹O₂.



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Process for the oxidation of organic substrates by means of singlet oxygen at high reaction temperatures

The invention relates to a process for the oxidation of organic substrates by means of singlet oxygen at high reaction temperatures.

The only singlet oxygen oxidation ($^1\text{O}_2\text{-Ox}$) which is at present carried out industrially is the photochemical $^1\text{O}_2\text{-Ox}$, in which the $^1\text{O}_2$ is generated photochemically. The disadvantages of this process are the high costs of the photochemical facilities required and a restricted life. The lamps required degenerate relatively quickly during the oxidation as a result of fouling of the glass surface. In addition, this process is not suitable for colored substrates. The process is actually suitable only for fine chemicals which are prepared on a relatively small scale. (La Chimica e l'Industria, 1982, Vol. 64, page 156)

For this reason, attempts have been made to find other process variants for $^1\text{O}_2\text{-Ox}$ which are suitable for the $^1\text{O}_2\text{-Ox}$ of hydrophobic organic substrates which are not soluble in water.

J. Am. Chem. Soc., 1968, **90**, 975, describes, for example, the classical "dark" $^1\text{O}_2\text{-Ox}$ in which $^1\text{O}_2$ is not generated photochemically but instead is generated chemically. Here, hydrophobic substrates are oxidized by means of a hypochlorite/ H_2O_2 system in a solvent mixture comprising water and an organic solvent. However, this process has found only a few synthetic applications, since many substrates are only sparingly soluble in the medium required. The opportunities for use are also fairly restricted because of secondary reactions between hypochlorite and substrate or solvent. In addition, a large part of the $^1\text{O}_2$ is deactivated in the gas phase. Furthermore, this process is not suitable for an industrial scale since an addition reaction of hypochlorite with H_2O_2 occurs in the organic medium and a large excess of H_2O_2 is required to suppress the

secondary reaction of substrate with hypochlorite. An additional disadvantage is the formation of stoichiometric amounts of salts.

One variant of "dark" $^1\text{O}_2$ -Ox which is not based on hypochlorite and should thus avoid part of the above disadvantages is known, for example, from J. Org. Chem., 1989, **54**, 726 or J. Mol. Cat., 1997, **117**, 439, according to which certain water-soluble organic substrates are oxidized by means of H_2O_2 and a molybdate catalyst in water as solvent. According to Membrane Lipid Oxid. Vol. II, 1991, 65, the $^1\text{O}_2$ -Ox of water-insoluble, organic substrates by means of the molybdate/ H_2O_2 system is difficult, because it was assumed that none of the customary solvents is able to maintain the molybdate-catalyzed disproportionation of H_2O_2 in water and $^1\text{O}_2$. However, the use of molybdenum catalysts is also associated with other disadvantages such as difficult recyclability or environmental pollution.

The use of molybdate-LDH catalysts for singlet oxygen oxidation is known from various literature references, for example from Adv. Synth. Catal. 2004, 346, 152-164, Chem. Commun., 1998, 267, or Chem. Eur. J. 2001, 7, 2547, but these do not have satisfactory selectivity and do not give satisfactory yields.

EP 1 169 281 discloses the singlet oxygen oxidation of organic substances in an organic solvent in the presence of a homogeneous catalyst based on molybdenum at from 0 to 50°C.

A further possible way of generating $^1\text{O}_2$ chemically is, for example, heating of triphenyl phosphite ozonide which is obtained from triphenyl phosphite and ozone. However, this method as described, for instance, in J. Org. Chem., Vol. 67, No 8, 2002, page 2418, can be employed only for mechanistic studies since triphenyl phosphite is an expensive and also hazardous chemical.

The base-catalyzed disproportionation of peracids forms not only $^1\text{O}_2$ but also further reactive compounds which lead to by-products.

It was accordingly an object of the present invention to make the oxidation of organic substrates by means of singlet oxygen ($^1\text{O}_2$) possible while avoiding accumulation of hydrogen peroxide in the reaction mixture and avoiding molybdenum-containing wastewater and also to discover a catalytic system for this purpose which has a high activity and selectivity.

This object has unexpectedly been able to be realised when the reaction is carried out at high reaction temperatures.

The present invention accordingly provides a process for the oxidation of organic substrates by means of singlet oxygen, wherein organic substrates which react with $^1\text{O}_2$ are admixed with 10-70% strength H_2O_2 in an organic solvent in the presence of a molybdenum-based catalyst at a pH of 9 – 14 and a temperature in the range from 50°C to the reflux temperature, whereupon the oxidation to the corresponding oxidation products occurs subsequent to the catalytic decomposition of H_2O_2 into water and $^1\text{O}_2$.

In the process of the invention, organic substrates are oxidized by means of singlet oxygen.

As organic substrates which react with $^1\text{O}_2$, it is possible to use the following compounds: olefins which have one or more, i.e. up to 10, preferably up to 6, particularly preferably up to 4, C=C double bonds; electron-rich aromatics such as C_6 - C_{50} -, preferably up to C_{30} -, particularly preferably up to C_{20} -phenols, polyalkylbenzenes, polyalkoxybenzenes; polycyclic aromatics having from 2 to 10, preferably up to 6, particularly preferably up to 4, aromatic rings; sulfides such as alkyl sulfides, alkenyl sulfides, aryl sulfides which are either monosubstituted or disubstituted on the sulfur atom and heterocycles having an O, N or S atom in the ring, for example C_4 - C_{50} -, preferably up to C_{30} -, particularly preferably up to C_{20} -furans, C_4 - C_{50} -, preferably up to C_{30} -,

particularly preferably up to C₂₀-pyrroles, C₄-C₆₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-thiophenes, C₄-C₆₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-indoles.

The substrates can have one or more substituents such as halogen (F, Cl, Br, I), cyanide, carbonyl groups, hydroxyl groups, C₁-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-alkoxy groups, C₁-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-alkyl groups, C₆-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-aryl groups, C₂-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-alkenyl groups, C₂-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-alkynyl groups, carboxylic acid groups, ester groups, amide groups, amino groups, nitro groups, silyl groups, silyloxy groups, sulfone groups, sulfoxide groups, etc. Furthermore, the substrates can be substituted by one or more NR₁R₂ radicals, where R₁ and R₂ can be identical or different and are each H; C₁-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-alkyl; formyl; C₂-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-acyl; C₇-C₅₀-, preferably up to C₃₀-, particularly preferably up to C₂₀-benzoyl; where R₁ and R₂ can together also form a ring, e.g. in a phthalimido group.

Examples of suitable substrates are: 2-butene; isobutene; 2-methyl-1-butene; 2-hexene; 1,3-butadiene; 2,3-dimethylbutene; D^{9,10}-octalin, 2-phthalimido-4-methyl-3-pentene; 2,3-dimethyl-1,3-butadiene; 2,4-hexadiene; 2-chloro-4-methyl-3-pentene; 2-bromo-4-methyl-3-pentene; 1-trimethylsilylcyclohexene; 2,3-dimethyl-2-butenyl-*para*-tolyl sulfone; 2,3-dimethyl-2-butenyl-*para*-tolyl sulfoxide; *N*-cyclohexenylmorpholine; 2-methyl-2-norbornene; terpinols; α -pinene; β -pinene; β -citronellol; ocimene; citronellol; geraniol; farnesol; terpinene; limonene; *trans*-2,3-dimethylacrylic acid; α -terpinene; isoprene; cyclopentadiene; 1,4-diphenylbutadiene; 2-ethoxybutadiene; 1,1'-dicyclohexenyl; cholesterol; ergosterol acetate; 5-chloro-1,3-cyclohexadiene; 3-methyl-2-buten-1-ol; 3,5,5-trimethylcyclohex-2-en-1-ol; phenol, 1,2,4-

trimethoxybenzene, 2,3,6-trimethylphenol, 2,4,6-trimethylphenol, 1,4-dimethylnaphthalene, furan, furfuryl alcohol, furfural, 2,5-dimethylfuran, isobenzofuran, 2,3-dimethylindole, dibenzyl sulfide, (2-methyl-5-*tert*-butyl)phenyl sulfide, etc.

The substrates are converted into the corresponding oxidation product by means of the oxidation according to the invention. Alkenes, (polycyclic) aromatics or heteroaromatics are converted, in particular, into hydroperoxides or peroxides which can react further under the reaction conditions to form alcohols, epoxides, acetals or carbonyl compounds such as ketones, aldehydes, carboxylic acids or esters if the hydroperoxide or the peroxide is not stable.

The oxidation according to the invention is carried out in an organic solvent. Suitable solvents are C₁-C₈-alcohols such as methanol, ethanol, propanol, *i*-propanol, butanol, *i*-butanol, *n*-butanol, *tert*-butanol, ethylene glycol, propylene glycol, acetone, 1,4-dioxane, tetrahydrofuran, formamide, *N*-methylformamide, dimethylformamide, sulfolane, propylene carbonate and mixtures thereof. Preference is given to using methanol, ethanol, propanol, *i*-propanol, ethylene glycol, propylene glycol, acetone, formamide, *N*-methylformamide or dimethylformamide, particularly preferably methanol, ethanol, ethylene glycol, propylene glycol, formamide or dimethylformamide, as solvent.

If desired, up to 25% of water can be mixed into the organic solvent. However, the addition of water gives no advantages in the reaction. Preference is therefore given to no water being added.

The appropriate substrate is taken up or dissolved in the solvent selected.

A molybdenum-based catalyst is then added to the solvent/substrate mixture.

The catalyst can here be used in the forms customary for $^1\text{O}_2$ oxidations, for example as oxide, oxo complex, nitrate, carboxylate, hydroxide, carbonate, chloride, etc., or as molybdate-LDH catalyst.

The amount of catalyst used depends on the substrate used and is in the range from 0.001 to 50 mol%, preferably from 0.1 to 10 mol%.

If appropriate, a base is added to the reaction mixture so that a pH of from 9 to 14, preferably from 10 to 13, is set.

Suitable bases are customary bases such as NaOH, KOH, etc.

10-70% strength, preferably 40-50% strength, H_2O_2 is subsequently added.

The consumption of H_2O_2 in the process of the invention is dependent on the substrate used. In the case of reactive substrates, from 2 to 3 equivalents of H_2O_2 are preferably required, while less reactive substrates are preferably reacted with from 3 to 10 equivalents of H_2O_2 .

The reaction temperature is in the range from 50°C to reflux temperature, preferably from 55°C to reflux temperature.

The higher the reaction temperature, the more quickly can the H_2O_2 be added, so that the reaction time can be significantly minimized.

The course of the reaction can be followed by means of UV spectroscopy, GC, DC, GC-MS or by means of HPLC.

After the reaction is complete, the reaction mixture is worked up.

The work-up of the reaction solution containing the oxidation product is carried out, if appropriate after reduction of the peroxides, by customary methods such as extraction, drying and isolation of the oxidation product.

The catalyst can, particularly when glycols are used as solvents, be recycled in a simple manner and be reused a number of times.

This can be carried out in a simple fashion by, after isolating the product, distilling off water from the remaining solution which contains the catalyst and reusing the resulting catalyst solution directly for a fresh reaction.

The process of the invention is particularly useful for the oxidation of substituted or unsubstituted 2,3-dimethylindole to prepare 2-(N-acetylamino)acetophenone. This variant for preparing 2-(N-acetylamino)acetophenone is novel and is therefore also provided by the present invention.

$^1\text{O}_2$ is generated in a simple and efficient way by means of the process of the invention.

The process of the invention gives the desired end products in high yields of up to 100% and high purity.

The process of the invention is simple to carry out and is best suited for the industrial scale since it can be carried out in simple multipurpose plants and with the aid of simple work-up steps and can be employed for a broad spectrum of substrates. A further advantage is the multiple reusability of the molybdenum catalyst used.

Example 1:

40.0 g of beta-citronellol were taken up in 240 ml of methanol and placed in a 500 ml double-walled vessel. 3.1 g of sodium molybdate were dissolved in 23.2 g of water and added to the solution, and the pH was then adjusted to pH=11.7 by means of sodium hydroxide.

The mixture was heated to 55°C and 2.9 equivalents of hydrogen peroxide (50% strength) were then metered in over a period of 6 hours.

After reduction of the peroxides, the reaction mixture was analyzed by gas chromatography.

Conversion: >95% based on citronellol used.

Product: (1:1 mixture of: 3,7-dimethyloct-7-ene-1,6-diol and 3,7-dimethyloct-5-ene-1,7-diol)

Example 2:

240.0 g of beta-citronellol were taken up in 1500 ml of ethylene glycol and 16.7 g of sodium molybdate and 30 g of water were added. (pH = 10.3). The solution was placed in a double-walled vessel and heated to 55°C. 313.1 g of hydrogen peroxide were added over a period of 6 hours (43.5 ml/h). After the reaction was complete, the reaction mixture was introduced into a sodium sulfite solution (193.5 g of sodium sulfite in 550 ml of water) and the peroxide solution was reduced at 60°C. The sodium sulfate was filtered off and the solution was extracted with MTBE (4 times with 500 ml each time). The MTBE extracts were then evaporated.

Yield: 266 g (1:1 mixture of: 3,7-dimethyloct-7-ene-1,6-diol and 3,7-dimethyloct-5-ene-1,7-diol)

Example 3

10.9 g of 2,3-dimethylindole were dissolved in 250 ml of ethylene glycol. 0.9 g of sodium molybdate and 1.5 g of water were added. The mixture was then heated to 50°C. 5.2 equivalents of hydrogen peroxide were metered in over a period of 17 hours. The peroxide-containing solution was reduced by means of sodium sulfite/water, the precipitated sodium sulfate was filtered off and the reaction mixture was extracted with MTBE (twice with 150 ml each time). The combined organic extracts were then evaporated. The residue was taken up in 30 ml of methanol and the product was crystallized out at 0°C.

This gave 2-(N-acetylamino)acetophenone having a purity of 97.5%.

Example 4:

240.0 g of beta-citronellol were taken up in 1500 ml of ethylene glycol and 16.7 g of sodium molybdate and 30 g of water were added. (pH = 10.3). The solution was placed in a double-walled vessel and heated to 70°C. 313.1 g of hydrogen peroxide were added over a period of 6 hours (43.5 ml/h). After the reaction was complete, the reaction mixture was introduced into a sodium sulfite solution (193.5 g of sodium sulfite in 550 ml of water) and the peroxide solution was reduced at 60°C. The sodium sulfate was filtered off and the solution was extracted with MTBE (4 times with 500 ml each time). The MTBE extracts were then evaporated.

Yield: 266 g (1:1 mixture of: 3,7-dimethyloct-7-ene-1,6-diol and 3,7-dimethyloct-5-ene-1,7-diol)

Example 5:

10.9 g of 2,3-dimethylindole were dissolved in 250 ml of ethylene glycol. 0.9 g of sodium molybdate and 1.5 g of water were added. The mixture was then heated to 70°C. 5.2 equivalents of hydrogen peroxide were metered in over a period of 17 hours. The peroxide-containing solution was reduced by means of sodium sulfite/water, the precipitated sodium sulfate was filtered off and the reaction mixture was extracted with MTBE (twice with 150 ml each time). The combined organic extracts were then evaporated. The residue was taken up in 30 ml of methanol and the product was crystallized out at 0°C.

This gave 2-(N-acetylamino)acetophenone having a purity of 97.5%.

Example 6:

1.6 g of citronellol were taken up in 9.6 ml of methanol and placed in a 20 ml double-walled vessel. 0.124 g of sodium molybdate was dissolved in 0.93 g of water and added. The pH was set to pH = 11.7 by means of 0.02 g of 5% strength NaOH and the solution was brought to reflux temperature (72°C methanol/water). 2.9 equivalents of 50% strength hydrogen peroxide were then added over a period of 30 minutes.

Analysis of the mixture after reduction of the peroxides indicated complete conversion (1:1 mixture of: 3,7-dimethyloct-7-ene-1,6-diol and 3,7-dimethyloct-5-ene-1,7-diol)

Example 7:

1.6 g of citronellol were taken up in 9.6 ml of methanol and placed in a 20 ml double-walled vessel. 0.124 g of sodium molybdate was dissolved in 0.93 g of water and added. The pH was set to pH = 11.7 by means of 0.02 g of 5% strength NaOH and the solution was brought to reflux temperature (73°C methanol/water). 2.9 equivalents of 50% strength hydrogen peroxide were then added all at once. After 5 minutes, the reaction mixture was reduced.

Analysis of the mixture after reduction of the peroxides indicated complete conversion (1:1 mixture of: 3,7-dimethyloct-7-ene-1,6-diol and 3,7-dimethyloct-5-ene-1,7-diol)

Example 8: Trial with recycling of glycol catalyst solution

240.0 g of beta-citronellol were taken up in 1500 ml of ethylene glycol and 16.7 g of sodium molybdate and 30 g of water were added. (pH = 10.3). The solution was placed in a double-walled vessel and heated to 70°C. 313.1 g of hydrogen peroxide were added over a period of 6 hours (43.5 ml/h). After the reaction was complete, the reaction mixture was introduced into a sodium sulfite solution (193.5 g of sodium sulfite in 550 ml of water) and the peroxide solution was reduced at 60°C. The sodium sulfate was filtered off and the solution was extracted with MTBE (4 times with 500 ml each time). The MTBE extracts were then evaporated.

Yield: 266 g (1:1 mixture of: 3,7-dimethyloct-7-ene-1,6-diol and 3,7-dimethyloct-5-ene-1,7-diol)

Recycling of the glycol phase with catalyst

The water was removed from the glycol/water phase by means of distillation or using a membrane.

240.0 g of beta-citronellol were added to the remaining 1556 g of ethylene glycol/catalyst/water. The yellow-orange solution was heated to 55°C and 313 g of hydrogen peroxide were added (43.5 ml/min). After the reaction was complete, the reaction mixture was introduced into a sodium sulfite solution (193.5 g of sodium sulfite in 550 ml of water) and the peroxide solution was reduced at 60°C. The sodium sulfate was filtered off and the solution was extracted with MTBE (4 times with 500 ml each time). The MTBE extracts were then evaporated.

Yield: 258 g (1:1 mixture of: 3,7-dimethyloct-7-ene-1,6-diol and 3,7-dimethyloct-5-ene-1,7-diol)

The glycol/water/catalyst phase could be processed as described above and reused.

Claims:

1. A process for the oxidation of organic substrates by means of singlet oxygen, wherein organic substrates which react with $^1\text{O}_2$ are admixed with 10-70% strength H_2O_2 in an organic solvent in the presence of a molybdenum-based catalyst at a pH of 9 – 14 and a temperature in the range from 50°C to the reflux temperature, whereupon the oxidation to the corresponding oxidation products occurs subsequent to the catalytic decomposition of H_2O_2 into water and $^1\text{O}_2$.
2. The process as claimed in claim 1, wherein olefins containing from 1 to 10 C=C double bonds; C₆-C₅₀-phenols, polyalkylbenzenes; polyalkoxybenzenes; polycyclic aromatics having from 2 to 10 aromatic rings; alkyl sulfides, alkenyl sulfides, aryl sulfides which are either monosubstituted or disubstituted on the sulfur atom and also C₄-C₆₀-heterocycles which have an O, N or S atom in the ring and may be unsubstituted or monosubstituted or multiply substituted by halogens, cyanide, carbonyl groups, hydroxyl groups, C₁-C₅₀-alkoxy groups, C₁-C₅₀-alkyl groups, C₆-C₅₀-acryl groups, C₂-C₅₀-alkenyl groups, C₂-C₅₀-alkynyl groups, carboxylic acid groups, ester groups, amide groups, amino groups, nitro groups, silyl groups, silyloxy groups, sulfone groups, sulfoxide groups or one or more NR¹R² radicals, where R₁ and R₂ can be identical or different and are each H; C₁-C₅₀-alkyl; formyl; C₂-C₅₀-acyl; C₇-C₅₀-benzoyl, where R¹ and R² can together also form a ring, are used as substrates which react with $^1\text{O}_2$.
3. The process as claimed in claim 1, wherein C₁-C₈-alcohols, acetone, 1,4-dioxane, tetrahydrofuran, formamide, N-methylformamide,

dimethylformamide, sulfolane, propylene carbonate or a mixture thereof is used as solvent.

4. The process as claimed in claim 3, wherein methanol, ethanol, propanol, i-propanol, ethylene glycol, propylene glycol, acetone, formamide, N-methylformamide or dimethylformamide is used as solvent.
5. The process as claimed in claim 1, wherein, depending on the substrate, from 0.001 to 50 mol% of catalyst are used.
6. The process as claimed in claim 1, wherein, depending on the substrate used, from 2 to 10 equivalents of H₂O₂ are used.
7. The process as claimed in claim 1, wherein the reaction temperature is in the range from 55°C to reflux temperature.
8. The process as claimed in claim 1, wherein, after the corresponding oxidation products have been isolated from the reaction mixture, water is removed from the catalyst-containing solution which remains and the catalyst/solvent mixture obtained in this way is used for further oxidations.
9. A process for the oxidation of substituted or unsubstituted 2,3-dimethylindole, wherein the substituted or unsubstituted 2,3-dimethylindole is admixed with 10-70% strength H₂O₂ in an organic solvent in the presence of a molybdenum-based catalyst at a pH of 9 – 14 and a temperature in the range from 50°C to the reflux temperature, whereupon the oxidation to substituted or unsubstituted 2-(N-acetylamino)acetophenone occurs subsequent to the catalytic decomposition of H₂O₂ into water and ¹O₂.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
 INV. C07B41/14 C07C29/48 C07C33/035 C07C231/14 C07C233/33

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C07B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/61524 A (DSM FINE CHEM AUSTRIA GMBH [AT]; AUBRY JEAN MARIE [FR]; RATAJ NARDELLO) 19 October 2000 (2000-10-19) cited in the application	1-8
Y	page 6 claim 7	9
X	EP 0 288 337 A (UNIV LILLE DROIT SANTE [FR]) 26 October 1988 (1988-10-26) cited in the application	1-8
Y	page 3, line 35 claim 9	9
E	WO 2006/108492 A (DSM FINE CHEM AUSTRIA GMBH [AT]; DE VOS DIRK [BE]; JACOBS PIERRE [BE];) 19 October 2006 (2006-10-19) page 6 claim 7	1-8

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	A	Publication date		Patent family member(s)	Publication date
WO 0061524	A	19-10-2000		AT 408546 B	27-12-2001
				AT 64799 A	15-05-2001
				AT 259764 T	15-03-2004
				AU 4290000 A	14-11-2000
				CA 2369589 A1	19-10-2000
				DE 50005331 D1	25-03-2004
				DK 1169281 T3	13-04-2004
				EP 1169281 A1	09-01-2002
				ES 2211533 T3	16-07-2004
				JP 2002541227 T	03-12-2002
				PT 1169281 T	31-05-2004
	US 6956137 B1	18-10-2005			
EP 0288337	A	26-10-1988	FR	2612512 A1	23-09-1988
WO 2006108492	A	19-10-2006	AT	501685 A1	15-10-2006