

Preparation of epoxides by means of aromatic peroxy-carboxylic acids

- 5 The present invention relates to an improved process for preparing epoxides, in particular alkylene oxides, from corresponding starting compounds, in particular from the corresponding olefins, by means of aromatic peroxy-carboxylic acids.
- 10 The epoxidation of olefins with peroxy-carboxylic acids, in particular with m-chloroperoxybenzoic acid, is a well established laboratory method for the synthesis of epoxides.

The method is extensively described in the chemical literature, for example by Y. Sawaki in S. Patai (ed.), Chem. Hydroxyl, Ether Peroxide Groups, p. 590-593 (1993) (1).

- However, the method is less suitable for preparing epoxides on a larger scale, since the peroxy-carboxylic acid is used in stoichiometric amounts and the resulting carboxylic acid has to be expensively regenerated by reaction with hydrogen peroxide.

- It is an object of the present invention to provide a process for preparing alkylene oxides by epoxidation of olefins with aromatic peroxy-carboxylic acids which permits a simple, safe and economical recycle of the resulting carboxylic acid into peroxy-carboxylic acid without use of hydrogen peroxide.

- We have found that this object is achieved by a process for preparing an epoxide from the corresponding olefin by means of an aromatic peroxy-carboxylic acid, which comprises a step A of epoxidizing the olefin and removing the resulting aromatic carboxylic acid from the epoxide, a step B of catalytically hydrogenating the removed aromatic carboxylic acid to the corresponding aromatic aldehyde, and a step C of oxidizing this aldehyde with oxygen or an oxygen-containing gas mixture back to the aromatic peroxy-carboxylic acid for re-use for preparing an epoxide.

- In principle, any olefin can be epoxidized in step A. Preference is given to olefins which carry not more than one electron-attracting substituent directly on the double bond. Particular preference is given to olefins without electron-attracting substituents on the double bond. Examples of useful olefins are linear or branched C₂-C₄₀-olefins, in particular C₃-C₂₄-olefins, or cyclic olefins, such as ethylene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 1-hexene, 1-heptene, 1-octene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 1-nonene,

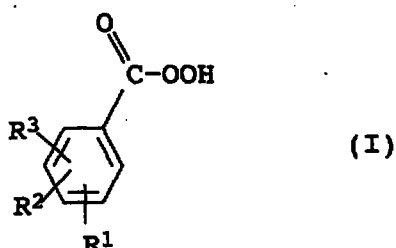
1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, C₂₀-olefin, C₂₂-olefin, C₂₄-olefin, C₂₈-olefin or C₃₀-olefin, cyclopropene, cyclobutene, cyclopentene, cyclohexene, cyclooctene, vinyl alkyl ethers such as vinyl methyl ether, vinyl ethyl ether or vinyl butyl ether, allyl chloride, allyl alcohol, vinyl acetate, vinyl propionate, styrene and also compounds having a plurality of olefinic double bonds such as 1,3-butadiene, isoprene, cyclopentadiene or cyclooctadiene. It is also possible to use olefin mixtures.

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The process of the present invention is particularly highly suitable for epoxidizing propene to propylene oxide.

Suitable aromatic peroxydicarboxylic acids are in particular compounds of the general formula I

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25 where R¹ to R³ are independently of one another hydrogen, C₁-C₆-alkyl, C₃-C₈-cycloalkyl, C₆-C₁₄-aryl, C₇-C₁₂-phenylalkyl, halogen, C₁-C₆-alkoxy, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryloxy or C₇-C₁₂-phenylalkoxy and one of R¹ to R³ can also be a further peroxydicarboxyl group or a carboxyl group.

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More particularly, the substituents R¹ to R³ have independently the following meanings:

- hydrogen;

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- C₁-C₆-alkyl, preferably C₁-C₄-alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl or n-hexyl, in particular methyl or tert-butyl;

40 - C₃-C₈-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl, in particular cyclopentyl or cyclohexyl or substituted C₃-C₈-cycloalkyl, in particular 1-methylcyclopentyl or 1-methylcyclohexyl;

45 - C₆-C₁₄-aryl such as phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl or 9-anthryl, in particular phenyl;

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- C₇-C₁₂-phenylalkyl such as 1-methyl-1-phenylethyl, benzyl, 1-phenylethyl, 2-phenylethyl, 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl, 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl or 4-phenylbutyl, in particular 1-methyl-1-phenylethyl;

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- halogen such as fluorine, chlorine or bromine; —

- C₁-C₆-alkoxy, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryloxy or C₇-C₁₂-phenylalkoxy, in which case the radicals on the oxygen atom have the above-innumeralated meanings of R¹ to R³ (with the exception of hydrogen);

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- peroxycarboxyl or carboxyl for one of R¹ to R³.

- 15 Preference is further given to those aromatic peroxy-carboxylic acids I which have one, two or three methyl groups as substituents R¹ to R³.

Examples of useful aromatic peroxy-carboxylic acids are in

- 20 particular peroxybenzoic acid, 2-methylperoxybenzoic acid (o-peroxytoluic acid), 3-methylperoxybenzoic acid (m-peroxytoluic acid), 4-methylperoxybenzoic acid (p-peroxytoluic acid), 2,4- and 3,5-dimethylperoxybenzoic acid, 2,4,6-trimethylperoxybenzoic acid, 4-tert-butylperoxybenzoic acid, 2-methyl-4-tert-butyl-
- 25 peroxybenzoic acid, 2,6-dimethyl-4-tert-butylperoxybenzoic acid, 2-, 3- or 4-ethylperoxybenzoic acid, 4-(1-methylcyclohexyl)-peroxybenzoic acid, 4-(1-methylcyclopentyl)peroxybenzoic acid, 4-phenylperoxybenzoic acid, 3-chloroperoxybenzoic acid, 4-methoxy- or 4-ethoxy-peroxybenzoic acid, 4-methoxy- or
- 30 4-ethoxy-2,6-dimethylperoxybenzoic acid, bisperoxyphthalic acid, monoperoxyphthalic acid, bisperoxyterephthalic acid and monoperoxyterephthalic acid. It is also possible to use mixtures of the aromatic peroxy-carboxylic acids mentioned. o-Peroxytoluic acid is particularly preferred.

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Step A of the process of the present invention is described in the literature as regards the epoxidation of olefins. The epoxidation is typically carried out as follows:

- 40 The aromatic peroxy-carboxylic acid, dissolved in a suitable solvent, is made to react with an olefin. The molar ratio of olefin to peroxy-carboxylic acid is within the range from 0.8:1 to 100:1, in particular from 1:1 to 20:1, especially from 1.5:1 to 5:1.

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The peroxy-carboxylic acid solution used can be an isolated peroxy-carboxylic acid dissolved in a solvent. It is preferable, however, to use directly the solution prepared in oxidation step C (with or without a prior purification step during which the peroxy-carboxylic acid remains in solution).

Suitable organic solvents for the peroxy-carboxylic acids in the epoxidation are ketones (e.g., acetone, butanone or tert-butyl methyl ketone), esters (e.g., methyl or ethyl acetate or methyl benzoate), nitro compounds (e.g., nitromethane or nitrobenzene), halogenated hydrocarbons (e.g., di- or trichloromethane, 1,1,1-trichloroethane or chlorobenzene), carbonates (e.g., dimethyl carbonate), urea derivatives (e.g., tetramethylurea), inorganic esters or amides (e.g., trimethyl phosphate or hexamethylphosphoramide), hydrocarbons (e.g., hexane or heptane), or alkylaromatics (e.g., benzene, toluene or xylene). However, it is particularly preferable to use the same solvent as in the oxidation of step C. Particularly preferred solvents for both steps are acetone, methyl acetate and ethyl acetate.

The epoxidation can be carried out at from -20 to 100°C, depending on solvent and olefin. If acetone is used as solvent and terminal olefins (e.g., 1-octene or propene) as substrate, temperatures from 25 to 80°C are preferred. Temperatures from 45 to 65°C are particularly preferred.

Surprisingly, at the relatively high temperature of 45°C or higher, the olefin is converted much more rapidly to the epoxide than any aromatic aldehyde still present from stage B is converted to carboxylic acid.

The aromatic carboxylic acids formed in step A from the aromatic peroxy-carboxylic acids I are separated from the oxidation products, in particular the alkylene oxides, by customary methods, for example by filtration, extraction or distillation.

The catalytic hydrogenation of the aromatic carboxylic acids in step B is preferably effected with hydrogen in the gas phase in the presence of a lanthanide/zirconia catalyst. Such catalysts are known for use as hydrogenation catalysts for converting aromatic carboxylic acids into the corresponding aldehydes from German Patent Application P 44 28 994.4 (2).

Step B of the process of the present invention is advantageously carried out as follows:

The hydrogenation of the aromatic carboxylic acid with hydrogen is carried out in the presence of a catalyst whose catalytically active material comprises from 60 to 99.9, in particular from 80 to 99.9, % by weight of zirconium oxide (ZrO_2) and from 0.1 to 40, 5 in particular from 0.1 to 20, % by weight of one or more elements of the lanthanides, is generally carried out at temperatures from 200 to 450°C, preferably from 250 to 400°C, in particular from 300 to 380°C, and pressures from 0.1 to 20 bar, preferably from 0.7 to 5 bar, in particular at atmospheric pressure. The temperature and 10 pressure required are dependent on the catalyst activity and the thermal stability of precursor and product.

Suitable catalysts include supported catalysts, preferably solid catalysts of zirconium oxide in cubic, tetragonal or monoclinic 15 phase, preferably in monoclinic phase, which have been doped with one or more elements of the lanthanide series. The catalytically active mass comprises preferably from 90 to 99.9% by weight, in particular from 92 to 99% by weight, of zirconium oxide and from 0.1 to 10% by weight, in particular from 1 to 8% by weight, of 20 one or more elements of the lanthanides, in particular lanthanum, cerium, praseodymium, neodymium, samarium, europium or mixtures thereof, especially lanthanum as lanthanum(III) oxide. The doping is generally effected by saturating the zirconium oxide with salt solutions (aqueous or alcoholic) of the lanthanides.

25 The catalyst may additionally include further dopants (e.g., chromium, iron, yttrium, hafnium, manganese) in amounts from 0.001 to 10% by weight. Preference is given to catalysts without such further additions.

30 The BET surface area of the zirconium oxide can vary within wide limits and is generally from 5 to 150 m²/g, preferably from 20 to 150 m²/g, in particular from 40 to 120 m²/g.

35 Catalysts of this type are produced in a conventional manner, for example by saturating preformed carrier elements such as pellets, balls or extrudates, drying and calcining.

The preferred supported catalysts are very active over a pro- 40 longed period. Deactivated catalysts can be regenerated by treatment with gases containing molecular oxygen, e.g., air, at temperatures from 350 to 500°C.

The weight hourly space velocity over the catalyst is held in 45 general within the range from 0.01 to 10, preferably from 0.01 to 3, kg of aromatic carboxylic acid per kg of catalyst per hour.

The hydrogen concentration in the feed gas depends on the carboxylic acid concentration. The molar ratio of hydrogen to aromatic carboxylic acid is in general within the range from 2:1 to 100:1, preferably within the range from 10:1 to 70:1. The
5 hydrogen can also come from formic acid used as source.

It can also be advantageous to add an inert diluent. Typically, nitrogen, water or gaseous reaction-inert compounds such as hydrocarbons, aromatics or ethers are employed.

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The reaction can be carried out in the gas phase, continuously as a fixed bed reaction with a fixed bed catalyst, for example in an upflow or downflow process, or as a fluidized bed reaction with the catalyst in the fluidized state. Preference is given to the
15 use of a fixed bed.

To increase the selectivity, by-products of the hydrogenation, for example alcohols, can be recycled into the synthesis.

20 The step B exit mixture, containing the aromatic aldehyde, passes with or without prior purification into step C where it is advantageously taken up in a suitable solvent and oxidized in the liquid phase with oxygen or an oxygen-containing gas mixture to the corresponding aromatic percarboxylic acid. This is preferably
25 done at temperatures from -10°C to 100°C and oxygen partial pressures from 0.001 to 100 bar.

DE-A-25 15 033 (3) discloses that p-tolualdehyde can be oxidized in acetone solution with air at 28°C and 30 bar without catalyst
30 to form p-peroxytoluic acid in a yield of about 80%. However, such high yields are only achieved with highly pure p-tolualdehyde and anhydrous acetone.

Step C of the process of the present invention is normally
35 carried out as follows:

The concentration of the aromatic aldehyde in the solvent can be from 1 to 75% by weight. Preferably it is from 5 to 35% by weight, in particular from 8 to 20% by weight.

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Oxygen or the oxygen-containing gas mixture can be made to react with the aromatic aldehyde either in gas form or as a solution, under atmospheric or superatmospheric pressure. The oxygen partial pressure is preferably from 0.01 to 30 bar, in particular
45 from 0.05 to 5 bar.

The oxidation can be carried out mono- or diphasically. Suitable reactors for the monophasic process are ones in which a solution of the aromatic aldehyde can be reacted with a solution of oxygen, under atmospheric or superatmospheric pressure, for example tubular reactors or flooded stirred tanks. Suitable reactors for the diphasic process ensure thorough gas-liquid mixing, such as bubble columns (with or without dividing walls or packing elements), stirred tanks (optionally equipped with sparging agitators and optionally arranged as a cascade) or trickle downflow reactors.

The reaction temperature is preferably from 0 to 60°C, in particular from 15 to 40°C.

The reaction time is chosen so as to produce an aldehyde conversion within the range from 40 to 100%. Preference is given to reaction times producing an aldehyde conversion within the range from 60 to 99%. Particular preference is given to reaction times producing an aldehyde conversion within the range from 75 to 95%.

The oxidation may additionally comprise a step of adding a stabilizer for the peroxy-carboxylic acid product, e.g., 8-hydroxyquinoline, dipicolinic acid or 2,6-dihydroxymethylpyridine.

Suitable organic solvents for step C are ketones (e.g., acetone, butanone or tert-butyl methyl ketone), esters (e.g., methyl or ethyl acetate or methyl benzoate), nitro compounds (e.g., nitromethane or nitrobenzene), halogenated hydrocarbons (e.g., di- or trichloromethane, 1,1,1-trichloroethane or chlorobenzene), carbonates (e.g., dimethyl carbonate), urea derivatives (e.g., tetramethylurea), inorganic esters or amides (e.g., trimethyl phosphate or hexamethylphosphoramide) or alkylaromatics (e.g., benzene, toluene or xylene). Preference is given to ketones, in particular acetone and tert-butyl methyl ketone, and esters, in particular methyl acetate, ethyl acetate and methyl benzoate.

The aromatic peroxy-carboxylic acid can either be isolated (by precipitation, for example), or else be re-used directly in step A without isolation (i.e., in solution).

It is surprising that o-tolualdehyde is faster and more selectively oxidizable than the isomeric m- and p-tolualdehydes.

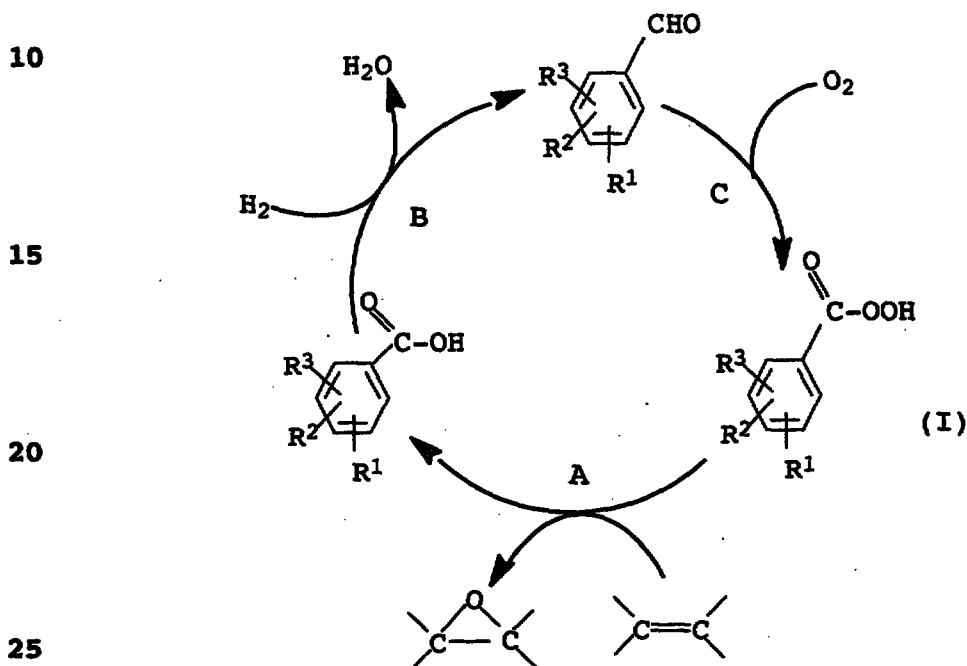
The process of the present invention has the advantage that the aromatic peroxy-carboxylic acid is regenerated without use of hydrogen peroxide after the oxidation/epoxidation. The aromatic

peroxycarboxylic acid acts only as an oxygen transfer agent and is not consumed to any practical extent. The stoichiometry of the overall process is in the case of epoxidation:



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A reaction scheme for the epoxidation using an aromatic peroxy-carboxylic acid I may be illustrated as follows:



Examples

30 Example 1

Epoxidation of 1-octene with p-peroxytoluic acid in acetone

50 g of an 8.3% strength by weight solution of p-peroxytoluic acid in acetone were admixed with 4.6 g (1.5 equivalents) of 1-octene and stirred at 40°C for 5 hours, when the conversion of the peroxyacid was about 90%. The octene oxide selectivity was about 80%, based on the peroxyacid, and >95%, based on 1-octene. The reaction temperature was raisable without significantly reducing the selectivity. At a reaction temperature of 60°C the peroxyacid conversion after 2 hours was about 90%. The octene oxide selectivity was unchanged compared with the run at 40°C.

Example 2

Epoxidation of propene with p-peroxytoluic acid in acetone

- 5 35 g of an 8.4% strength by weight solution of p-peroxytoluic acid in acetone were charged initially to a 50 ml glass autoclave, 2.4 g of propene (3 equivalents) were injected, and the contents were stirred at 60°C for 4.5 hours. The peroxyacid conversion was 94%. The propylene oxide selectivity based on the
10 peroxyacid was >95%.

Example 3

Epoxidation of 1-octene with o-peroxytoluic acid in acetone

- 15 100 g of an 11.3% strength by weight solution of o-peroxytoluic acid in acetone were admixed with 16.8 g of 1-octene (2 equivalents) and stirred at 60°C. After 1 hour the peroxyacid conversion was 92%. The octene oxide selectivity was 97%, based on o-peroxytoluic acid.

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Example 4

Preparation of the catalyst for the hydrogenation in step B

- Monoclinic ZrO_2 (BET surface area: 40 - 85 m^2/g) in the form of
25 tablets (catalysts A and E) or extrudates (catalysts B, C and D) was saturated with an aqueous solution of the lanthanide element nitrate (or lanthanide element nitrates) by thorough mixing and the mixture was held at room temperature for 2 hours. The catalyst was then dried at 120°C for 15 hours and then heat-treated at
30 from 400 to 500°C for from 2 to 4 hours.

The catalysts thus prepared had the following lanthanide contents:

- Catalyst A (surface area: 67 m^2/g): 3% by weight of lanthanum;
35 Catalyst B (surface area: 46 m^2/g): 3% by weight of praseodymium;
Catalyst C (surface area: 46 m^2/g): 3% by weight of cerium;
Catalyst D (surface area: 46 m^2/g): 3% by weight of lanthanides (distribution: 48.2% by weight of CeO_2 , 26.4% by weight of La_2O_3 , 5.7% by weight of Pr_2O_3 and 19.7% by weight of Nd_2O_3);
40 Catalyst E (surface area: 53 m^2/g): 3% by weight of lanthanum.

Examples 5a to 5i

Hydrogenation of 4-substituted aromatic carboxylic acids

- 45 Per hour, from 4 to 8 g of aromatic carboxylic acid, without a solvent or dissolved in tetrahydrofuran (THF), were passed into a vaporizer (<300°C) and carried from there by 100 l/h of hydrogen

through 100 g of catalyst in a trickle downflow. The gaseous reaction effluent was condensed in cold traps and analyzed by gas chromatography. The carboxylic acids used and the results are summarized in Table 1.

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Table 1

Ex. No.	Catalyst	Carboxylic acid R ¹⁾	Conc. of carboxylic acid [wt.%] ²⁾	Reactor temp. [°C]	Yield of aldehyde [%]	Conversion [%]	Selectivity [%]
10 5a	A	H	100	340	98	100	98
5b	A	H	20	350	98	100	98
15 5c	A	methyl	100	340	96	99	97
5d	A	t-butyl	100	340	90	94	96
5e	A	t-butyl	20	340	93	97	96
5f	A	methyl	10	350	77	99	78
5g	B	H	100	360	95	100	95
20 5h	C	H	100	360	96	100	96
5i	D	H	100	360	97	99	98

1) substituent in position 4 of the carboxylic acid: -COOH

25 2) in solvent (THF); 100% by weight indicates pure carboxylic acid, without solvent

Example 6

Hydrogenation of 3-methylbenzoic acid

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Hydrogen at 100 l/h was used to vaporize 8 g/h of 3-methylbenzoic acid (as melt) and pass it at 360°C in the downflow direction through 100 g of catalyst E. The gaseous reaction effluent was condensed in cold traps and analyzed by gas chromatography. The

35 yield of 3-methylbenzaldehyde was 92% (conversion 99%).

Example 7

Hydrogenation of 2-methylbenzoic acid

40 Hydrogen at 200 l/h was used to vaporize 8 g/h of 2-methylbenzoic acid (as melt) and pass it at 350°C in the downflow direction through 100 g of catalyst E. The gaseous reaction effluent was condensed in cold traps and analyzed by gas chromatography. The

45 yield of 2-methylbenzaldehyde was 93% (conversion 99%).

Examples 8a to 8e

Oxidation of aromatic aldehydes with air to peroxycarboxylic acids in acetone

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A solution of aromatic aldehyde (10% strength by weight in acetone) was oxidized with air at 30°C in a four-neck flask equipped with gas inlet tube, high-speed Hoesch stirrer, a thermometer and a reflux condenser. The peroxyacid concentration was determined by iodometry. Other components can be determined by gas chromatography (after reduction of the peroxyacid with tributyl phosphite). The aldehydes used and the results are summarized in Table 2.

15 Table 2

Ex. No.	Aldehyde	Reaction time	Conversion of aldehyde	Peroxyacid selectivity	
		[h]	[%]	[%]	
20	8a	benzaldehyde	2	34	77
	8b	p-tolualdehyde	7	84	83
	8c	m-tolualdehyde	6	90	82
	8d	o-tolualdehyde	4	80	93
25	8e	p-methoxy-benzaldehyde	1	37	72

Example 9

Oxidation of p-tolualdehyde in methyl acetate

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Example 8b was repeated with methyl acetate instead of acetone as solvent. After 7 hours of reaction the aldehyde conversion was 62%. The p-peroxytoluic acid selectivity was 69%.

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Example 10

Oxidation of o-tolualdehyde with oxygen under superatmospheric pressure

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A 10% strength by weight solution of o-tolualdehyde in acetone was oxidized at 5 bar and 30°C with pure oxygen in a magnetically stirred 10 ml glass autoclave. After 1.5 hours the aldehyde conversion was about 80%. o-Peroxytoluic acid had been formed with a selectivity of >90%. The rest was chiefly o-toluic acid. By-products such as phthalide, toluene, o-cresol and o-cresol formate

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were formed with a selectivity of only about 0.2%.

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The oxidation could also be carried out in more concentrated solutions. The oxidation of a 20% strength by weight solution of o-tolualdehyde (30°C, 5 bar oxygen, 3 hours reaction time) yielded the corresponding peroxyacid with a selectivity of about 93%
5 (aldehyde conversion: 90%).

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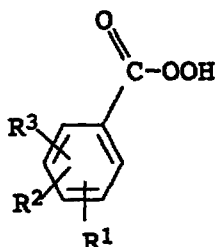
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We claim:

1. A process for preparing an alkylene oxide from the corresponding olefin by means of an aromatic peroxydicarboxylic acid, which comprises a step A of epoxidizing the olefin and removing the resulting aromatic dicarboxylic acid from the alkylene oxide, a step B of catalytically hydrogenating the removed aromatic dicarboxylic acid to the corresponding aromatic aldehyde, and a step C of oxidizing this aldehyde with oxygen or an oxygen-containing gas mixture back to the aromatic peroxydicarboxylic acid for re-use for epoxidizing an olefin.
2. A process as claimed in claim 1 wherein propene is epoxidized to propylene oxide.
3. A process as claimed in claim 1 or 2 wherein the aromatic peroxydicarboxylic acid used is a compound of the general formula I



(I)

- where R¹ to R³ are independently of one another hydrogen, C₁-C₆-alkyl, C₃-C₈-cycloalkyl, C₆-C₁₄-aryl, C₇-C₁₂-phenylalkyl, halogen, C₁-C₆-alkoxy, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryloxy or C₇-C₁₂-phenylalkoxy and one of R¹ to R³ can also be a further peroxydicarboxyl group or a carboxyl group.
4. A process as claimed in any of claims 1 to 3 wherein the step B catalytic hydrogenation of the aromatic dicarboxylic acid is carried out with hydrogen in the gas phase in the presence of a lanthanide/zirconia catalyst.
 5. A process as claimed in any of claims 1 to 3 wherein the step C oxidation of the aromatic aldehyde is carried out in the liquid phase in a suitable solvent at temperatures from -10°C to 100°C and oxygen partial pressures from 0.001 to 100 bar.



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6. A process as claimed in any of claims 1 to 3 wherein the epoxidation is carried out in a solvent.

5 7. A process as claimed in claim 1 wherein the epoxidation and the oxidation of the aldehyde are carried out in the same solvent.

8. A process as claimed in claim 7 wherein the solvent used is acetone, methyl acetate or ethyl acetate.

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9. A process as claimed in claim 3 wherein the peroxycarboxylic acid used is o-peroxytoluic acid.

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