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(54) **PROCESS FOR THE PREPARATION OF ALPHA-FUNCTIONALIZED KETONES**

VERFAHREN ZUR HERSTELLUNG VON ALPHA-FUNKTIONALISIERTEN KETONEN

PROCÉDÉ DE PRÉPARATION DE CÉTONES FONCTIONNALISÉES EN ALPHA

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- **CHENGQUN CHEN ET AL: "An Efficient Method for the Synthesis of [alpha]-Hydroxyalkyl Aryl Ketones", SYNTHESIS, vol. 2008, no. 20, 25 September 2008 (2008-09-25), pages 3205-3208, XP055411187, STUTTGART, DE. ISSN: 0039-7881, DOI: 10.1055/s-0028-1083149**
- **AMOLAK C. JAIN ET AL: "Synthesis of Isopentenylated 4-Hydroxy-3-Methoxycoumarins and [omega]-Methyl-[omega]-Desacetyl Ripariochromene-B", SYNTHETIC COMMUNICATIONS, vol. 6, no. 2, 1 January 1976 (1976-01-01), pages 147-166, XP055433183, PHILADELPHIA, PA; US ISSN: 0039-7911, DOI: 10.1080/00397917608072625**

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- Karanj Ketone ET AL: "SYNTHESIS OF BENZO-FURAN DERIVATIVES-I", Tetrahedron, 1 January 1958 (1958-01-01), pages 203-210, XP055433184, Retrieved from the Internet: URL:<http://www.sciencedirect.com/science/article/pii/0040402058880412/pdf?md5=b5edb9f1a95a148b6422fba8eebc8af4&pid=1-s2.0-0040402058880412-main.pdf>

Description**Field of the invention**

- 5 **[0001]** The present invention refers to a process for the preparation of an α -functionalized ketone, an α -functionalized ketone obtained by said process.

Background of the invention

- 10 **[0002]** Photopolymerization processes have attained major importance in a large number of applications, for example in overprint coatings, printing inks, in the manufacture of electronic printed circuit boards and printing plates, and in the coating of various substrates, such as wood, plastics, paper, glass or metal, due their tremendous advantages over conventional hardening systems. One advantage of photo-curing by UV irradiation in the presence of photoinitiators is the great speed. However, the speed is heavily dependent on the photoinitiator used. Among the most effective photoinitiators are α -hydroxylated ketones as described e.g. in German Patent No. 2,722,264 and US patent application US 4,740,624. Further methods for the α -functionalization of ketones are described e.g. in Gary Jing Chuang et al., "A Dinuclear Palladium Catalyst for α -Hydroxylation of Carbonyls with O₂", J. Am. Chem. Soc. 133, 1760-1762 (2011). Chengqun Chen et al. "An Efficient Method for the Synthesis of α -Hydroxyalkyl Aryl Ketones", Synthesis 2008, No. 20, 3205-3208; Marek Koprowski et al., "Asymmetric oxidation of enol phosphates to α -hydroxy ketones by (salen)manganese(III) complex; Effects of the substitution pattern of enol phosphates on the stereochemistry of oxygen transfer", Tetrahedron 62 12363-12374 (2006); Franklin A. Davis et al., "Oxidation of Silyl Enol Ethers Using 2-Sulfonyloxaziridines; Synthesis of α -Siloxy Epoxides and α -Hydroxy Carbonyl Compounds", J. Org. Chem. 52, 954-955 (1987); Yu-Feng Liang et al., "Highly Efficient C-H Hydroxylation of Carbonyl Compounds with Oxygen under Mild Conditions", Angew. Chem. 2014, 126, 558-562; Yu-Feng Liang et al., "I₂- or NBS-Catalyzed Highly Efficient α -Hydroxylation of Ketones with Dimethyl Sulfoxide", Org. Lett. 17, 876-879 (2015); Bang-Chi Chen et al., " α -hydroxylation of enolates and silyl enol ethers", Organic Reactions, Vol. 62, 2003, published by John Wiley & Sons, Inc.

- 25 **[0003]** US 4 740 624 A discloses a process for the preparation of α -hydroxylated ketones carried out by contacting the corresponding alkyl aryl ketone under phase-transfer conditions with a tetrahalogenomethane and an alkali metal hydroxide. WO 2006/034066 A1 discloses a multi-step process for synthesizing an α -amino ketone compound, which comprises reacting an aromatic thioether ketone with chlorine gas, reacting the obtained chlorinated compound either with a primary or secondary amine in the presence of a Lewis acid, or with an alkali alcoholate and subsequently with a primary or secondary amine. The above mentioned reference of Chengqun Chen et al. describes the exposure of alkyl aryl ketones to a mixture of potassium peroxymonosulfate and trifluoroacetic anhydride in the presence of a catalytic amount of iodobenzene to obtain α -hydroxyalkyl aryl ketones.

- 35 **[0004]** However, the processes used for the preparation of the α -hydroxylated ketones have a number of disadvantages. In particular, it is to be noted that the α -hydroxylated ketones are prepared by multiple step reactions resulting in a great variety of by-products which reduce the yield and purity of the desired α -hydroxylated ketone. Furthermore, elaborate purification steps are required. Accordingly, the well-known processes of the prior art are quite complex, require costly chemicals or catalysts as well as are time- and chemical-consuming.

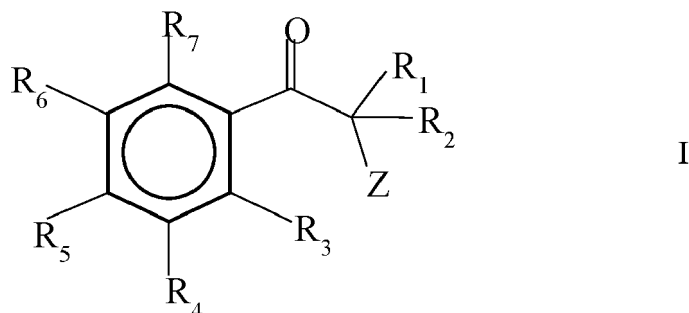
- 40 **[0005]** Despite of numerous efforts, a simple and cheap process for this kind of functionalization is still missing. Therefore, there is a continuous need in the art for providing a process for the preparation of α -functionalized ketones avoiding the foregoing disadvantages. In particular, it is desirable to provide a process for the preparation of α -functionalized ketones which avoids a multiple step reaction. Furthermore, it is desirable to provide a process for the preparation of α -functionalized ketones using cheap and safe starting materials. Furthermore, it is desirable to provide a process for the preparation of α -functionalized ketones which avoids elaborate purification steps for obtaining the desired α -functionalized ketones. In addition thereto, it is desirable to provide a process for the preparation of α -functionalized ketones which avoids the formation of excessive by-products and thus increases the yield and purity of the desired α -functionalized ketones. Furthermore, there is still a need for a process which allows the preparation of α -functionalized ketones that have not been accessible by the processes of the prior art up to now.

- 50 **[0006]** Accordingly, it is an object of the present invention to provide a process for the preparation of α -functionalized ketones. Furthermore, it is an object of the present invention to provide a one-pot process for the preparation of α -functionalized ketones. It is an even further object of the present invention to provide a process for the preparation of α -functionalized ketones using cheap starting materials and without elaborate purification steps for obtaining the desired α -functionalized ketones. It is an even further object of the present invention to provide a process for the preparation of α -functionalized ketones which increases the yield and purity of the desired α -functionalized ketones. It is another object of the present invention to provide a process which allows the preparation of α -functionalized ketones that have not been accessible by the processes of the prior art up to now. It is a further object of the present specification to provide new α -functionalized ketones that can be used as photoinitiators.

Summary of the invention

[0007] The foregoing and other objects are solved by the subject-matter of the present invention. The present invention provides a process for the preparation of an α -functionalized ketone according to claim 1.

[0008] According to the present invention, a process for the preparation of an α -functionalized ketone of the general formula I is provided,

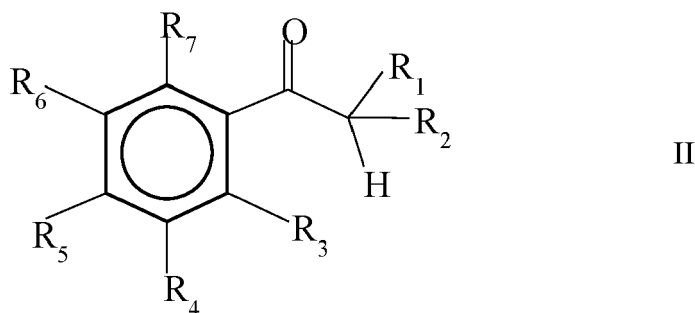


wherein R_1 and R_2 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, linear or branched C_2 - C_8 -alkenyl, C_5 - C_8 -cycloalkenyl, linear or branched C_2 - C_8 -alkynyl, C_6 - C_{14} -aryl or form C_3 - C_{12} -cyloalkyl or C_5 - C_{12} -cycloalkenyl together with the connecting C atom;

R_3 , R_4 , R_5 , R_6 and R_7 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_6 - C_{14} -aryl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy, $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_6 - C_{14} -aryl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, or two adjacent R form an aromatic system together with the benzene ring of formula I;

Z is selected from OR_9 , NHR_9 and $NR_{10}R_{11}$ with R_9 , R_{10} and R_{11} being independently selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_6 - C_{14} -aryl, C_7 - C_{15} -arylalkyl, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy, C_9 - C_{15} -alkenylarylalkyl; or R_{10} and R_{11} form a C_3 - C_9 -alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O;

characterized in that a ketone of the general formula II



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and R_7 are as defined above, is contacted under phase-transfer conditions with an at least partially halogenated C_2 - C_8 -alkane and/or C_2 - C_8 -alkene, and i) a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C_1 - C_8 -alkoxide, earth alkali metal C_1 - C_8 -alkoxide and mixtures thereof, or ii) a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C_1 - C_8 -alkoxide, earth alkali metal C_1 - C_8 -alkoxide and mixtures thereof together with the protonated form of Z as defined above.

[0009] The inventors surprisingly found out that such a process is suitable for the preparation of α -functionalized ketones in a one-pot process by using cheap starting materials and avoiding elaborate purification steps for obtaining the desired α -functionalized ketones. The process for the preparation of α -functionalized ketones thus increases the yield and purity of the desired α -functionalized ketones. Furthermore, the process allows the preparation of α -function-

alized ketones that have not been accessible by the processes of the prior art up to now and thus also results in new α -functionalized ketones that can be used as photoinitiators.

[0010] Advantageous embodiments of the inventive process are defined in the corresponding sub-claims.

[0011] According to one embodiment, R_1 and R_2 are the same.

[0012] According to another embodiment, R_1 and R_2 are selected from H and linear or branched C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl and most preferably linear C_1 - C_3 -alkyl.

[0013] According to yet another embodiment, R_1 and R_2 are different and are independently selected from H and linear or branched C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl and most preferably linear C_1 - C_3 -alkyl.

[0014] According to one embodiment, R_1 and R_2 form C_4 - C_{10} -cycloalkyl, preferably C_4 - C_8 -cycloalkyl, and most preferably C_6 -cycloalkyl, together with the connecting C atom.

[0015] According to another embodiment, that R_3 , R_4 , R_5 , R_6 and R_7 are the same.

[0016] According to yet another embodiment, R_3 , R_4 , R_5 , R_6 and R_7 are selected from H and linear or branched C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl and most preferably linear C_1 - C_3 -alkyl.

[0017] According to one embodiment, R_3 , R_4 , R_5 , R_6 and R_7 are different and at least one of them is selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy; C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylarylalkoxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom.

[0018] According to another embodiment, one of R_3 , R_4 , R_5 , R_6 and R_7 is linear or branched C_2 - C_8 -alkenyl, preferably C_2 - C_6 -alkenyl and most preferably C_2 - C_3 -alkenyl; C_1 - C_8 -alkoxy, preferably C_1 - C_6 -alkoxy and most preferably C_1 - C_3 -alkoxy; C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy; C_9 - C_{15} -alkenylarylalkoxy, preferably C_9 - C_{12} -alkenylarylalkoxy and most preferably C_9 - C_{10} -alkenylarylalkoxy; or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom; and the remaining ones are independently selected from H and linear or branched C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl and most preferably linear C_1 - C_3 -alkyl. According to yet another embodiment, two or three of R_3 , R_4 , R_5 , R_6 and R_7 are linear or branched C_2 - C_8 -alkenyl, preferably C_2 - C_6 -alkenyl and most preferably C_2 - C_3 -alkenyl; C_1 - C_8 -alkoxy, preferably C_1 - C_6 -alkoxy and most preferably C_1 - C_3 -alkoxy; C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy; and C_9 - C_{15} -alkenylarylalkoxy, preferably C_9 - C_{12} -alkenylarylalkoxy and most preferably C_9 - C_{10} -alkenylarylalkoxy, and the remaining ones are independently selected from H and linear or branched C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl and most preferably linear C_1 - C_3 -alkyl.

[0019] According to one embodiment, that R_3 and R_4 or R_4 and R_5 form an aromatic system together with the benzene ring of formula I, preferably a bicyclic, tricyclic or tetracyclic aromatic system, more preferably an aromatic system selected from a naphthyl, anthracenyl and phenanthrenyl system.

[0020] According to another embodiment, one of the remaining R is linear or branched C_2 - C_8 -alkenyl, preferably C_2 - C_6 -alkenyl and most preferably C_2 - C_3 -alkenyl; C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy; and C_9 - C_{15} -alkenylarylalkoxy, preferably C_9 - C_{12} -alkenylarylalkoxy and most preferably C_9 - C_{10} -alkenylarylalkoxy; and the remaining ones are independently selected from H and linear or branched C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl and most preferably linear C_1 - C_3 -alkyl.

[0021] According to yet another embodiment, Z is OR_9 with R_9 being selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy and C_9 - C_{15} -alkenylarylalkoxy, preferably R_9 is H or Z is $NR_{10}R_{11}$ with R_{10} and R_{11} being independently selected from H, linear or branched C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, C_6 - C_{14} -aryl, or R_{10} and R_{11} form a C_3 - C_6 -alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, preferably R_{10} and R_{11} form a C_5 - C_6 -alicyclic system together with the connecting N atom and one or more carbon atoms are replaced with O.

[0022] According to one embodiment, the at least partially halogenated C_2 - C_8 -alkane and/or C_2 - C_8 -alkene is fully halogenated, preferably the at least partially halogenated C_2 - C_8 -alkane and/or C_2 - C_8 -alkene is selected from hexachloroethane, tetrachloroethylene and mixtures thereof.

[0023] According to another embodiment, the base is selected from the group comprising sodium hydroxide; lithium hydroxide; potassium hydroxide; sodium C_1 - C_6 -alkoxide, preferably sodium C_1 - C_4 -alkoxide and most preferably sodium C_1 - C_2 -alkoxide; lithium C_1 - C_6 -alkoxide, preferably lithium C_1 - C_4 -alkoxide and most preferably lithium C_1 - C_2 -alkoxide; potassium C_1 - C_6 -alkoxide, preferably potassium C_1 - C_4 -alkoxide and most preferably potassium C_1 - C_2 -alkoxide; and mixtures thereof; or the base is selected from sodium C_1 - C_6 -alkoxide, preferably sodium C_1 - C_4 -alkoxide and most preferably sodium C_1 - C_2 -alkoxide; potassium C_1 - C_6 -alkoxide, preferably potassium C_1 - C_4 -alkoxide and most preferably potassium C_1 - C_2 -alkoxide, together with the protonated form of Z as defined above.

[0024] According to yet another embodiment, the base is in form of an aqueous solution or the base is provided in an organic solvent, preferably the organic solvent is selected from the group comprising methanol, ethanol, n-propanol,

tert.-butanol, dichloromethane, tetrachloroethylene, tetrahydrofuran, ethyl acetate, acetone, N,N-dimethylformamide, dimethyl sulfoxide, dioxane, such as 1,3-dioxane or 1,4-dioxane, 1,2-dimethoxyethane, diethyleneglycol dimethyl ether, triethyleneglycol dimethyl ether and mixtures thereof.

[0025] According to one embodiment, the process is carried out at a temperature of at least 30 °C, preferably in the range from 30 to 120 °C, more preferably in the range from 40 to 100 °C, and most preferably in the range from 40 to 90 °C.

[0026] According to another embodiment, the process is carried out in an organic solvent, preferably the organic solvent is selected from the group comprising methanol, ethanol, n-propanol, tert.-butanol, dichloromethane, tetrachloroethylene, tetrahydrofuran, ethyl acetate, acetone, N,N-dimethylformamide, dimethyl sulfoxide, dioxane, such as 1,3-dioxane or 1,4-dioxane, 1,2-dimethoxyethane, diethyleneglycol dimethyl ether, triethyleneglycol dimethyl ether and mixtures thereof.

[0027] According to yet another embodiment, the process is carried out in the presence of a phase-transfer catalyst, preferably the phase-transfer catalyst is selected from a quaternary ammonium salt, tetraalkylphosphonium chloride, tetraalkylphosphonium bromide and mixtures thereof, preferably the phase-transfer catalyst is a tetraalkylammonium salt or a trialkylaryl ammonium salt, more preferably the phase-transfer catalyst is selected from the group comprising benzyltrimethylammonium hydroxide, benzyltriethylammonium chloride, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium hydrogensulfate, tetrabutylammonium hydroxide, methyltrioctylammonium chloride, cetyl pyridinium and mixtures thereof.

[0028] According to one embodiment, the α -functionalized ketone is obtained in an one-pot reaction.

[0029] According to another embodiment, the process further comprises a step of

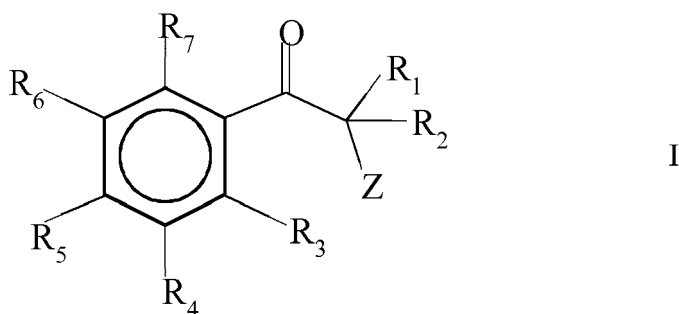
- i) separating the obtained organic and aqueous phases, and/or
- ii) extracting the obtained aqueous phase with the organic solvent used in the process and combining the obtained organic phases, and/or
- iii) acidifying the obtained organic phase to a pH of 3 to 6.5.

[0030] According to a further aspect of the present specification, an α -functionalized ketone obtained by a process, as defined herein, is provided.

[0031] In the following, the details and preferred embodiments of the inventive process for the preparation of an α -functionalized ketone will be described in more detail.

Detailed description of the invention

[0032] A process for the preparation of an α -functionalized ketone is provided. It is appreciated that an α -functionalized ketone of the general formula I is prepared,



wherein R_1 and R_2 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, linear or branched C_2 - C_8 -alkenyl, C_5 - C_8 -cycloalkenyl, linear or branched C_2 - C_8 -alkynyl, C_6 - C_{14} -aryl or form C_3 - C_{12} -cycloalkyl or C_5 - C_{12} -cycloalkenyl together with the connecting C atom;

R_3 , R_4 , R_5 , R_6 and R_7 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_6 - C_{14} -aryl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy, $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_6 - C_{14} -aryl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, or two adjacent R form an aromatic system together with the benzene ring of formula I;

[0033] Z is selected from OR_9 , NHR_9 and $NR_{10}R_{11}$ with R_9 , R_{10} and R_{11} being independently selected from H, linear

or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryl, C₇-C₁₅-arylalkyl, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, C₉-C₁₅-alkenylarylalkyl; or R₁₀ and R₁₁ form a C₃-C₉-alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O.

[0034] As regards R₁ and R₂ in the general formula I, it is to be noted that they can be the same or different. Preferably, R₁ and R₂ are the same or different and are independently selected from H, linear or branched C₁-C₈-alkyl, C₃-C₈-cycloalkyl, linear or branched C₂-C₈-alkenyl, C₅-C₈-cycloalkenyl, linear or branched C₂-C₈-alkynyl, C₆-C₁₄-aryl or form C₃-C₁₂-cycloalkyl or C₅-C₁₂-cycloalkenyl together with the connecting C atom.

[0035] The term "linear or branched C₁-C₈-alkyl" in the meaning of the present invention refers to a linear or branched chain alkyl group having 1 to 8 carbon atoms, and includes, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, pentyl, isopentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl and 1,1,3,3-tetramethylbutyl.

[0036] The term "C₃-C₈-cycloalkyl" in the meaning of the present invention refers to a cyclic alkyl having 3 to 8 carbon atoms, and includes, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl.

[0037] The term "C₅-C₈-cycloalkenyl" in the meaning of the present invention refers to a cyclic alkenyl having 3 to 8 carbon atoms, and includes, for example, cyclopentenyl, cyclohexenyl, and cycloheptenyl.

[0038] The term "linear or branched C₂-C₈-alkenyl" in the meaning of the present invention refers to a linear or branched chain alkenyl group having 2 to 8 carbon atoms, and includes, for example, ethenyl, propenyl such as 2-propenyl, butenyl, pentenyl, hexenyl, heptenyl and octenyl. The term "alkenyl" in the meaning of the present invention includes the cis and trans isomers.

[0039] The term "linear or branched C₂-C₈-alkynyl" in the meaning of the present invention refers to a linear or branched chain alkynyl group having 2 to 8 carbon atoms, and includes, for example, ethynyl, propynyl such as 1-propynyl or 2-propynyl, e.g. propargyl, butynyl, pentynyl, hexynyl, heptynyl and octynyl.

[0040] The term "C₆-C₁₄-aryl" in the meaning of the present invention refers to a group containing one or more 6-membered unsaturated hydrocarbon ring(s), wherein the unsaturation is represented formally by conjugated double bonds and which may optionally be substituted at one or more carbon atoms of such ring(s) by independently selected alkyl groups. Thus, the term "C₆-C₁₄-aryl" preferably includes (unsubstituted) C₆-C₁₀-aryl and C₆-C₁₄-arylalkyl. Suitable examples include, for example, phenyl, naphthyl, methylphenyl, dimethoxyphenyl, 5-isopropyl-2-methylphenyl, methylphenyl, ethylphenyl, dimethylphenyl, t-butylphenyl, methylnaphthyl and dimethylnaphthyl.

[0041] The term "form C₃-C₁₂-cycloalkyl together with the connecting C atom" in the meaning of the present invention refers to a mono-, bi- or tricyclic alkyl having 3 to 12 carbon atoms, and includes, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, norbornyl and adamantyl.

[0042] The term "form C₅-C₁₂-cycloalkenyl together with the connecting C atom" in the meaning of the present invention refers to a mono-, bi- or tricyclic alkenyl having 5 to 12 carbon atoms, and includes, one or more, preferably one, double bond(s). Suitable examples include, for example, cyclopentenyl, cyclohexenyl, cyclohexadienyl and cycloheptenyl. It is appreciated that the double bond of the C₅-C₁₂-cycloalkenyl is located such that an α,β -unsaturated carbonyl compound is not formed. Thus, R₁ and R₂ in the general formula I can form C₅-C₁₂-cycloalkenyl together with the connecting C atom with the proviso that no α,β -unsaturated carbonyl compound is formed.

[0043] In one embodiment, R₁ and R₂ are the same or different and are independently selected from H, linear or branched C₁-C₈-alkyl, C₃-C₈-cycloalkyl, or form C₃-C₁₂-cycloalkyl together with the connecting C atom. Preferably, R₁ and R₂ are the same or different and are independently selected from H or linear or branched C₁-C₈-alkyl.

[0044] For example, R₁ and R₂ are the same. In this embodiment, R₁ and R₂ are preferably selected from H, linear or branched C₁-C₈-alkyl, C₃-C₈-cycloalkyl, linear or branched C₂-C₈-alkenyl, C₅-C₈-cycloalkenyl, linear or branched C₂-C₈-alkynyl, C₆-C₁₄-aryl or form C₃-C₁₂-cycloalkyl or C₅-C₁₂-cycloalkenyl together with the connecting C atom.

[0045] In one embodiment, R₁ and R₂ are the same and are H.

[0046] In another embodiment, R₁ and R₂ are the same and are linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl. For example, R₁ and R₂ are the same and are linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl. It is especially preferred that R₁ and R₂ are the same and are C₁- or C₂-alkyl, e.g. C₁-alkyl.

[0047] In another embodiment, R₁ and R₂ form C₃-C₁₂-cycloalkyl together with the connecting C atom. For example, R₁ and R₂ form C₄-C₁₀-cycloalkyl, preferably C₄-C₈-cycloalkyl, even more preferably C₄-C₆-cycloalkyl, and most preferably C₅- or C₆-cycloalkyl, e.g. C₆-cycloalkyl, together with the connecting C atom.

[0048] In another embodiment, R₁ and R₂ are the same and are linear or branched C₂-C₈-alkenyl, e.g. linear C₂-C₈-alkenyl. For example, R₁ and R₂ are the same and are linear or branched C₂-C₆-alkenyl, e.g. linear C₂-C₆-alkenyl, preferably linear or branched C₂-C₄-alkenyl, e.g. linear C₂-C₄-alkenyl, and most preferably linear or branched C₂- or C₃-alkenyl, e.g. linear C₂- or C₃-alkenyl. It is especially preferred that R₁ and R₂ are the same and are C₃-alkenyl.

[0049] In another embodiment, R₁ and R₂ are the same and are linear or branched C₂-C₈-alkynyl, e.g. linear C₂-C₈-alkynyl. For example, R₁ and R₂ are the same and are linear or branched C₂-C₆-alkynyl, e.g. linear C₂-C₆-alkynyl, preferably linear or branched C₂-C₄-alkynyl, e.g. linear C₂-C₄-alkynyl, and most preferably linear or branched C₂- or C₃-alkynyl,

e.g. linear C₂- or C₃-alkynyl. It is especially preferred that R₁ and R₂ are the same and are C₃-alkynyl.

[0050] In another embodiment, R₁ and R₂ are the same and are linear or branched C₆-C₁₄-aryl, e.g. (unsubstituted) C₆-C₁₀-aryl or C₆-C₁₄-alkylaryl. For example, R₁ and R₂ are the same and are (unsubstituted) C₆- or C₁₀-aryl. Alternatively, R₁ and R₂ are the same and are C₈-C₁₂-alkylaryl.

[0051] In another embodiment, R₁ and R₂ form C₅-C₁₂-cycloalkenyl together with the connecting C atom. For example, R₁ and R₂ form C₅-C₁₀-cycloalkenyl, preferably C₅-C₈-cycloalkenyl and most preferably C₅- or C₆-cycloalkenyl, e.g. C₆-cycloalkenyl, together with the connecting C atom.

[0052] If R₁ and R₂ are the same, it is preferred that R₁ and R₂ are linear or branched C₁-C₈-alkyl, preferably linear C₁-C₈-alkyl, or form C₃-C₁₂-cycloalkyl, preferably C₅- or C₆-cycloalkyl, together with the connecting C atom. More preferably, R₁ and R₂ are linear or branched C₁-C₈-alkyl, preferably linear C₁-C₈-alkyl, or form C₃-C₁₂-cycloalkyl. Most preferably, R₁ and R₂ are linear or branched C₁-C₈-alkyl, preferably linear C₁-C₈-alkyl. Alternatively, R₁ and R₂ are different. In this embodiment, R₁ and R₂ are preferably independently selected from H, linear or branched C₁-C₈-alkyl, C₃-C₈-cycloalkyl, linear or branched C₂-C₈-alkenyl, C₅-C₈-cycloalkenyl, linear or branched C₂-C₈-alkynyl or C₆-C₁₄-aryl. For example, R₁ and R₂ are different and are selected from H and linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, linear or branched C₂-C₈-alkenyl, e.g. linear C₂-C₈-alkenyl, preferably linear or branched C₂-C₆-alkenyl, e.g. linear C₂-C₆-alkenyl, more preferably linear or branched C₂-C₄-alkenyl, e.g. linear C₂-C₄-alkenyl, even more preferably linear or branched C₂- or C₃-alkenyl, e.g. linear C₂- or C₃-alkenyl and most preferably C₃-alkenyl, and linear or branched C₂-C₈-alkynyl, e.g. linear C₂-C₈-alkynyl, preferably linear or branched C₂-C₆-alkynyl, e.g. linear C₂-C₆-alkynyl, more preferably linear or branched C₂-C₄-alkynyl, e.g. linear C₂-C₄-alkynyl, even more preferably linear or branched C₂- or C₃-alkynyl, e.g. linear C₂- or C₃-alkynyl and most preferably C₃-alkynyl, e.g. propargyl. In one embodiment, R₁ and R₂ are different and are selected from H and linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl. In one embodiment, R₁ and R₂ are different and are selected from H and C₁- or C₂-alkyl, preferably C₂-alkyl.

[0053] If R₁ and R₂ are different, R₁ or R₂ is preferably H and the remaining R₁ or R₂ is preferably linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, even more preferably linear C₁-C₃-alkyl, and most preferably C₁- or C₂-alkyl, e.g. C₂-alkyl.

[0054] Preferably, R₁ and R₂ are the same.

[0055] The α -functionalized ketone of the general formula I further comprises residues R₃, R₄, R₅, R₆ and R₇. It is appreciated that R₃, R₄, R₅, R₆ and R₇ can be the same or different. Furthermore, R₃, R₄, R₅, R₆ and R₇ are the same or different and are independently selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₆-C₁₄-aryl, C₃-C₈-cycloalkoxy, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, N(R₈)₂ or SR₈ with R₈ being selected from linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₆-C₁₄-aryl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom, or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, or two adjacent R form an aromatic system together with the benzene ring of formula I.

[0056] The term "C₁-C₈-alkoxy" in the meaning of the present invention means that the alkoxy moiety has a linear or branched chain alkyl having 1 to 8 carbon atoms, and includes, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, tertiary butoxy, pentyloxy, hexyloxy, heptyloxy and octyloxy.

[0057] The term "C₂-C₈-alkenyloxy" in the meaning of the present invention means that the alkenyloxy moiety has a linear or branched chain alkenyl having 2 to 8 carbon atoms, and includes, for example, ethenyloxy, propenyloxy, butenyloxy, pentenyloxy, hexenyloxy, heptenyloxy and octenyloxy.

[0058] The term "C₃-C₈-cycloalkoxy" in the meaning of the present invention means that the cycloalkoxy moiety has a cyclic alkyl having 3 to 8 carbon atoms, and includes, for example, cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, and cycloheptyloxy.

[0059] The term "C₇-C₁₅-arylalkoxy" in the meaning of the present invention means that the alkoxy moiety has a linear or branched chain alkyl having 1 to 8 carbon atoms, preferably 1 or 2 carbon atoms, which is connected to C₆-C₁₄-aryl.

[0060] The term "C₇-C₁₅-arylalkyl" in the meaning of the present invention means that the alkyl moiety is a linear or branched chain alkyl having 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms, which is connected to C₆-C₁₄-aryl.

[0061] The term "C₉-C₁₅-alkenylarylalkoxy" in the meaning of the present invention means that the alkoxy moiety has a linear or branched chain alkyl having 1 to 8 carbon atoms, preferably 1 or 2 carbon atoms, which is connected to C₆-C₁₄-aryl, preferably C₆-aryl, which is further connected to linear or branched C₂-C₈-alkenyl, preferably C₂-alkenyl. Preferably, the alkoxy and alkenyl moieties are connected in para-position of the aryl moiety.

[0062] In one embodiment, R₃, R₄, R₅, R₆ and R₇ are the same. In this embodiment, R₃, R₄, R₅, R₆ and R₇ are the same and are selected from H and linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl. For example, R₃, R₄, R₅, R₆

and R_7 are the same and are linear or branched C_1 - C_6 -alkyl, e.g. linear C_1 - C_6 -alkyl, preferably linear or branched C_1 - C_4 -alkyl, e.g. linear C_1 - C_4 -alkyl, and most preferably linear C_1 - C_3 -alkyl, e.g. linear C_1 - or C_2 -alkyl. It is especially preferred that R_3 , R_4 , R_5 , R_6 and R_7 are the same and are H.

[0063] Alternatively, R_3 , R_4 , R_5 , R_6 and R_7 are different. In this embodiment, R_3 , R_4 , R_5 , R_6 and R_7 are different and at least one of them is selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom.

[0064] The term "at least one" in the meaning of the present invention means that one or more of R_3 , R_4 , R_5 , R_6 and R_7 is selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom.

[0065] For example, one or two or three of R_3 , R_4 , R_5 , R_6 and R_7 is/are selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom. For example, one or two of R_3 , R_4 , R_5 , R_6 and R_7 is/are selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom. Preferably, one of R_3 , R_4 , R_5 , R_6 and R_7 is selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom.

[0066] If R_3 , R_4 , R_5 , R_6 and R_7 are different and at least one of them is selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom, it is preferred that the remaining ones are selected from H and linear or branched C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl and most preferably linear C_1 - C_3 -alkyl, e.g. C_1 - or C_2 -alkyl. For example, R_3 , R_4 , R_5 , R_6 and R_7 are different and at least one of them is selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom and the remaining ones are H.

[0067] In one embodiment, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_9 - C_{15} -alkenylaryloxy or $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl or linear or branched C_2 - C_8 -alkenyl or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom.

[0068] For example, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is linear or branched C_2 - C_8 -alkenyl, e.g. linear C_2 - C_8 -alkenyl; preferably linear or branched C_2 - C_6 -alkenyl, e.g. linear C_2 - C_6 -alkenyl; and most preferably C_2 - C_3 -alkenyl, e.g. C_2 - or C_3 -alkenyl; and the remaining ones are H.

[0069] Alternatively, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy, e.g. C_3 - or C_4 -alkenyloxy, especially C_3 -alkenyloxy; and the remaining ones are H.

[0070] In one embodiment, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy, e.g. C_3 - or C_4 -alkenyloxy, especially C_3 -alkenyloxy; and the remaining ones are independently selected from H and linear or branched C_1 - C_8 -alkyl, e.g. linear C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, e.g. linear C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl, e.g. linear C_1 - C_4 -alkyl, and most preferably linear C_1 - C_3 -alkyl, e.g. C_1 - or C_2 -alkyl, especially C_1 -alkyl.

[0071] For example, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy, e.g. C_3 - or C_4 -alkenyloxy, especially C_3 -alkenyloxy; and two of the remaining ones are H and two of the remaining ones are linear or branched C_1 - C_8 -alkyl, e.g. linear C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, e.g. linear C_1 - C_6 -alkyl, more preferably linear or branched C_1 - C_4 -alkyl, e.g. linear C_1 - C_4 -alkyl, and most preferably linear C_1 - C_3 -alkyl, e.g. C_1 - or C_2 -alkyl, especially C_1 -alkyl.

[0072] Alternatively, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is C_9 - C_{15} -alkenylaryloxy, preferably C_9 - C_{12} -alkenylaryloxy and most preferably C_9 - C_{10} -alkenylaryloxy; and the remaining ones are H.

[0073] Alternatively, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl, e.g. linear C_1 - C_8 -alkyl, preferably linear or branched C_1 - C_6 -alkyl, e.g. linear C_1 - C_6 -alkyl, preferably linear or branched C_1 - C_4 -alkyl, e.g. linear C_1 - C_4 -alkyl, and most preferably linear C_1 - C_3 -alkyl, e.g. C_1 - or C_2 -alkyl, especially C_1 -alkyl; and the remaining ones are H.

[0074] Alternatively, R_3 , R_4 , R_5 , R_6 and R_7 are different and one of them is $N(R_8)_2$ with R_8 forming a C_3 - C_9 -alicyclic

system, preferably a C₃-C₇-alicyclic system, more preferably a C₄-C₆-alicyclic system and most preferably a C₅- or C₆-alicyclic system, together with the connecting N atom; and the remaining ones are H. Optionally one or more carbon atoms are replaced with O. Preferably, R₃, R₄, R₅, R₆ and R₇ are different and one of them is N(R₈)₂ with R₈ forming a C₃-C₉-alicyclic system, preferably a C₃-C₇-alicyclic system, more preferably a C₄-C₆-alicyclic system and most preferably a C₅- or C₆-alicyclic system, together with the connecting N atom, wherein one or more, preferably one, carbon atoms are replaced with O; and the remaining ones are H.

[0075] If R₃, R₄, R₅, R₆ and R₇ are different and one of them is selected from linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₉-C₁₅-alkenylarylalkoxy or N(R₈)₂ or SR₈ with R₈ being selected from linear or branched C₁-C₈-alkyl or linear or branched C₂-C₈-alkenyl or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom, it is preferred that R₅ is selected from linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₉-C₁₅-alkenylarylalkoxy or N(R₈)₂ or SR₈ with R₈ being selected from linear or branched C₁-C₈-alkyl or linear or branched C₂-C₈-alkenyl or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom.

[0076] Thus, if R₃, R₄, R₅, R₆ and R₇ are different and one of them is selected from linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₉-C₁₅-alkenylarylalkoxy or N(R₈)₂ or SR₈ with R₈ being selected from linear or branched C₁-C₈-alkyl or linear or branched C₂-C₈-alkenyl or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom, it is preferred that this group is in para-position to the keto group.

[0077] In an alternative embodiment, R₃, R₄, R₅, R₆ and R₇ are different and two or three of them are linear or branched C₂-C₈-alkenyl, e.g. linear C₂-C₈-alkenyl, preferably linear or branched C₂-C₆-alkenyl, e.g. linear C₂-C₆-alkenyl, and most preferably C₂-C₃-alkenyl; C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy, and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl.

[0078] For example, R₃, R₄, R₅, R₆ and R₇ are different and two of them are linear or branched C₂-C₈-alkenyl, e.g. linear C₂-C₈-alkenyl, preferably linear or branched C₂-C₆-alkenyl, e.g. linear C₂-C₆-alkenyl, and most preferably C₂-C₃-alkenyl; C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy, and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl, preferably the remaining ones are H.

[0079] Alternatively, R₃, R₄, R₅, R₆ and R₇ are different and two of them are C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy; and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl, preferably the remaining ones are H.

[0080] In one embodiment, R₃, R₄, R₅, R₆ and R₇ are different and three of them are C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy, and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl, preferably the remaining ones are H.

[0081] If two or three of R₃, R₄, R₅, R₆ and R₇ are linear or branched C₂-C₈-alkenyl, e.g. linear C₂-C₈-alkenyl, preferably linear or branched C₂-C₆-alkenyl, e.g. linear C₂-C₆-alkenyl, and most preferably C₂-C₃-alkenyl; C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy, it is appreciated that preferably R₄ and/or R₅ and/or R₆ are linear or branched C₂-C₈-alkenyl, e.g. linear C₂-C₈-alkenyl, preferably linear or branched C₂-C₆-alkenyl, e.g. linear C₂-C₆-alkenyl, and most preferably C₂-C₃-alkenyl; C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy.

[0082] In one embodiment, R₃ and R₄ or R₄ and R₅ form an aromatic system together with the benzene ring of general formula I, preferably a bicyclic, tricyclic or tetracyclic aromatic system, more preferably an aromatic system selected from a naphthyl, anthracenyl and phenanthrenyl system. The aromatic system is preferably a bicyclic aromatic system, most preferably naphthyl.

[0083] For example, R₄ and R₅ form an aromatic system together with the benzene ring of general formula I, preferably

a bicyclic aromatic system, most preferably naphthyl; and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl, preferably H.

[0084] It is appreciated that one of the remaining R may be linear or branched C₂-C₈-alkenyl, preferably C₂-C₆-alkenyl and most preferably C₂-C₃-alkenyl; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy; and the remaining ones may be independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl, preferably H.

[0085] In one embodiment, R₄ and R₅ form an aromatic system together with the benzene ring of general formula I, preferably a bicyclic aromatic system, most preferably naphthyl, and R₃ is linear or branched C₂-C₈-alkenyl, preferably C₂-C₆-alkenyl and most preferably C₂-C₃-alkenyl; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy; and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl, preferably H. For example, R₄ and R₅ form an aromatic system together with the benzene ring of general formula I, preferably a bicyclic aromatic system, most preferably naphthyl, and R₃ is C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy; and the remaining ones are H.

[0086] The α -functionalized ketone of the general formula I further comprises Z being selected from OR₉, NHR₉ and NR₁₀R₁₁ with R₉, R₁₀ and R₁₁ being independently selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryl, C₇-C₁₅-arylalkyl, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, C₉-C₁₅-alkenylarylalkyl; or R₁₀ and R₁₁ form a C₃-C₉-alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O.

[0087] In one embodiment, Z is OR₉ with R₉ being selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₇-C₁₅-arylalkoxy and C₉-C₁₅-alkenylarylalkoxy, preferably R₉ is H or Z is NR₁₀R₁₁ with R₁₀ and R₁₁ being independently selected from H, linear or branched C₁-C₈-alkyl, C₃-C₈-cycloalkyl, C₆-C₁₄-aryl, or R₁₀ and R₁₁ form a C₃-C₆-alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, preferably R₁₀ and R₁₁ form a C₅-C₆-alicyclic system together with the connecting N atom and one or more carbon atoms are replaced with O.

[0088] Preferably, Z is OR₉ with R₉ being H or NR₁₀R₁₁ with R₁₀ and R₁₁ forming a C₅-C₆-alicyclic system, preferably a C₆-alicyclic system, together with the connecting N atom and one or more carbon atoms, preferably one carbon atom, is/are replaced with O.

[0089] An especially preferred α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are selected from linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₃, R₄, R₅, R₆ and R₇ are the same and are H, and Z is OR₉ with R₉ being H.

[0090] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are C₁-alkyl; R₃, R₄, R₅, R₆ and R₇ are the same and are H, and Z is OR₉ with R₉ being H.

[0091] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ form C₃-C₁₂-cycloalkyl, preferably C₄-C₁₀-cycloalkyl, more preferably C₄-C₈-cycloalkyl, even more preferably C₄-C₆-cycloalkyl, and most preferably C₅- or C₆-cycloalkyl, e.g. C₆-cycloalkyl, together with the connecting C atom; R₄, R₅, R₆ and R₇ are the same and are H, and Z is OR₉ with R₉ being H.

[0092] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are selected from linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₄, R₅, R₆ and R₇ are the same and are H, and Z is NR₁₀R₁₁ with R₁₀ and R₁₁ forming a C₅-C₆-alicyclic system, preferably a C₆-alicyclic system.

[0093] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are selected from linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₄, R₅, R₆ and R₇ are the same and are H, and Z is NR₁₀R₁₁ with R₁₀ and R₁₁ forming a C₅-C₆-alicyclic system, preferably a C₆-alicyclic system, together with the connecting N atom and one or more, preferably one, carbon atoms are replaced with O.

[0094] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are C₁-alkyl; R₄, R₅, R₆ and R₇ are the same and are H, and Z is NR₁₀R₁₁ with R₁₀ and R₁₁ forming a C₅-C₆-alicyclic system, preferably a C₆-alicyclic system, together with the connecting N atom and one or more, preferably one, carbon atoms are replaced with O.

linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; and Z is OR₉ with R₉ being H.

[0104] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are C₁-alkyl; R₃, R₄, R₅, R₆ and R₇ are different and one of them, preferably R₅, is C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy, e.g. C₃- or C₄-alkenyloxy, especially C₃-alkenyloxy; and two of the remaining ones, preferably R₃ and R₇, are H and two of the remaining ones, preferably R₄ and R₆, are linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl, especially C₁-alkyl; and Z is OR₉ with R₉ being H.

[0105] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are selected from linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₃, R₄, R₅, R₆ and R₇ are different and three of them, preferably R₃ and R₄ and R₅, are C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy, and the remaining ones, preferably R₆ and R₇ are H; and Z is OR₉ with R₉ being H.

[0106] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are C₁-alkyl; R₃, R₄, R₅, R₆ and R₇ are different and three of them, preferably R₃ and R₄ and R₅, are C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy, and the remaining ones, preferably R₆ and R₇ are H; and Z is OR₉ with R₉ being H.

[0107] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are different and are selected from H and linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₃, R₄, R₅, R₆ and R₇ are different and two of them, preferably R₄ and R₅, are C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy, especially C₁-alkoxy; and the remaining ones, preferably R₃, R₆ and R₇, are H and Z is OR₉ with R₉ being H.

[0108] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are different and are H and C₂-alkyl; R₃, R₄, R₅, R₆ and R₇ are different and two of them, preferably R₄ and R₅, are C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy, especially C₁-alkoxy; and the remaining ones, preferably R₃, R₆ and R₇, are H and Z is OR₉ with R₉ being H.

[0109] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are different and are selected from H and linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₃, R₄, R₅, R₆ and R₇ are different and one of them, preferably R₅, is N(R₈)₂ with R₈ forming a C₃-C₉-alicyclic system, preferably a C₃-C₇-alicyclic system, more preferably a C₄-C₆-alicyclic system and most preferably a C₅- or C₆-alicyclic system, together with the connecting N atom, wherein one or more, preferably one, carbon atoms are replaced with O; and the remaining ones, preferably R₃, R₄, R₆ and R₇, are H and Z is OR₉ with R₉ being H.

[0110] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are different and are H and C₂-alkyl; R₃, R₄, R₅, R₆ and R₇ are different and one of them, preferably R₅, is N(R₈)₂ with R₈ forming a C₃-C₉-alicyclic system, preferably a C₃-C₇-alicyclic system, more preferably a C₄-C₆-alicyclic system and most preferably a C₅- or C₆-alicyclic system, together with the connecting N atom, wherein one or more, preferably one, carbon atoms are replaced with O; and the remaining ones, preferably R₃, R₄, R₆ and R₇, are H and Z is OR₉ with R₉ being H.

[0111] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are selected from linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₄ and R₅ form an aromatic system together with the benzene ring of general formula I, preferably a bicyclic aromatic system, most preferably naphthyl; and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl, preferably H, and Z is OR₉ with R₉ being H.

[0112] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are C₁-alkyl; R₄ and R₅ form an aromatic system together with the benzene ring of general formula I, preferably a bicyclic aromatic system, most preferably naphthyl; and the remaining ones are H and Z is OR₉ with R₉ being H.

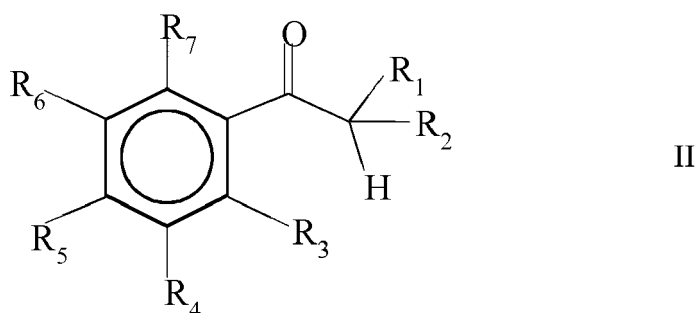
[0113] Alternatively, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are selected from linear or branched C₁-C₈-alkyl, e.g. linear C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, e.g. linear C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl, e.g. linear C₁-C₄-alkyl, and most preferably linear C₁-C₃-alkyl, e.g. C₁- or C₂-alkyl, especially C₁-alkyl; R₄ and R₅ form an aromatic system together with the benzene ring

of general formula I, preferably a bicyclic aromatic system, most preferably naphthyl; and one of the remaining R, preferably R₃, is linear or branched C₂-C₈-alkenyl, preferably C₂-C₆-alkenyl and most preferably C₂-C₃-alkenyl; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy and the remaining ones are H, and Z is OR₉ with R₉ being H.

[0114] For example, the α -functionalized ketone of the general formula I is a ketone, wherein R₁ and R₂ are the same and are C₁-alkyl; R₄ and R₅ form an aromatic system together with the benzene ring of general formula I, preferably a bicyclic aromatic system, most preferably naphthyl; and one of the remaining R, preferably R₃, is C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy and the remaining ones are H, and Z is OR₉ with R₉ being H.

[0115] It is appreciated that the α -functionalized ketone of the general formula I is prepared by a specific process, namely a one-pot process, avoiding elaborate purification steps for obtaining the desired α -functionalized ketones. The yield and purity of the desired α -functionalized ketones are thus significantly increased. Furthermore, the process allows the preparation of α -functionalized ketones that have not been accessible by the processes of the prior art up to now and thus also results in new α -functionalized ketones that can be used as photoinitiators.

[0116] The process is characterized in that a ketone of the general formula II



wherein R₁, R₂, R₃, R₄, R₅, R₆ and R₇ are as defined above, is contacted under phase-transfer conditions with an at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene, and a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof, or a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof together with the protonated form of Z as defined above.

[0117] With regard to the definition of the α -functionalized ketone, the R₁, R₂, R₃, R₄, R₅, R₆ and R₇ and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the α -functionalized ketone of the general formula I obtained by process of the present invention.

[0118] In one embodiment, the ketone of the general formula II is contacted under phase-transfer conditions with the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene, and the base together with the protonated form of Z.

[0119] With regard to the definition of Z and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the α -functionalized ketone of the general formula I obtained by the process of the present invention. Accordingly, it is to be noted that the skilled person will readily understand what is meant by the wording "protonated form of Z".

[0120] However, the process is preferably carried out by contacting the ketone of the general formula II under phase-transfer conditions with the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene, and the base together with the protonated form of Z, if Z in general formula I is NHR₉ or NR₁₀R₁₁ with R₉, R₁₀ and R₁₁ being independently selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryl, C₇-C₁₅-arylalkyl, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, C₉-C₁₅-alkenylarylalkyl; or R₁₀ and R₁₁ form a C₃-C₉-alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O.

[0121] Accordingly, the protonated form of Z is preferably HNHR₉ or HNR₁₀R₁₁ with R₉, R₁₀ and R₁₁ being independently selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryl, C₇-C₁₅-arylalkyl, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, C₉-C₁₅-alkenylarylalkyl; or R₁₀ and R₁₁ form a C₃-C₉-alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O.

[0122] It is preferred that the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is an at least partially halogenated C₂-C₆-alkane and/or C₂-C₆-alkene, more preferably an at least partially halogenated C₂-C₄-alkane and/or

C₂-C₄-alkene. For example, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is an at least partially halogenated C₂- or C₃-alkane and/or C₂- or C₃-alkene, e.g. an at least partially halogenated C₂-alkane and/or C₂-alkene.

[0123] The at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene may be at least partially chlorinated and/or brominated. For example, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is at least partially chlorinated or brominated. Alternatively, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is at least partially chlorinated and brominated, and thus is a mixed halogenated C₂-C₈-alkane and/or C₂-C₈-alkene.

[0124] Preferably, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is at least partially chlorinated.

[0125] In one embodiment, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is fully halogenated. Preferably, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is a fully halogenated C₂-C₆-alkane and/or C₂-C₆-alkene, more preferably a fully halogenated C₂-C₄-alkane and/or C₂-C₄-alkene. For example, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is a fully halogenated C₂- or C₃-alkane and/or C₂- or C₃-alkene.

[0126] For example, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene may be fully chlorinated and/or brominated. For example, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is fully chlorinated or brominated. Alternatively, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is fully chlorinated and brominated, and thus is a mixed halogenated C₂-C₈-alkane and/or C₂-C₈-alkene.

[0127] Preferably, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is fully chlorinated.

[0128] In one embodiment, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is selected from hexachloroethane, tetrachloroethylene, pentachloropropane, hexabromoethane, tetrabromoethylene, pentabromopropane and mixtures thereof. Preferably, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is hexachloroethane, tetrachloroethylene and mixtures thereof. For example, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is hexachloroethane or tetrachloroethylene.

[0129] In one embodiment, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is hexachloroethane and tetrachloroethylene.

[0130] Another essential component of the process is the addition of a base. It is a requirement of the present invention that the base is selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof, or a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof together with the protonated form of Z as defined above.

[0131] In one embodiment, the base is selected from the group comprising sodium hydroxide; lithium hydroxide; potassium hydroxide; sodium C₁-C₆-alkoxide, preferably sodium C₁-C₄-alkoxide and most preferably sodium C₁-C₂-alkoxide; lithium C₁-C₆-alkoxide, preferably lithium C₁-C₄-alkoxide and most preferably lithium C₁-C₂-alkoxide; potassium C₁-C₆-alkoxide, preferably potassium C₁-C₄-alkoxide and most preferably potassium C₁-C₂-alkoxide; and mixtures thereof. Preferably, the base is selected from the group comprising sodium hydroxide and sodium C₁-C₆-alkoxide, preferably sodium C₁-C₄-alkoxide and most preferably sodium C₁-C₂-alkoxide. Most preferably, the base is sodium hydroxide. This embodiment is especially preferred if Z in general formula I is OR₉, with R₉, being H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryl, C₇-C₁₅-arylalkyl, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, C₉-C₁₅-alkenylarylalkyl.

[0132] Alternatively, the base is selected from sodium C₁-C₆-alkoxide, preferably sodium C₁-C₄-alkoxide and most preferably sodium C₁-C₂-alkoxide; lithium C₁-C₆-alkoxide, preferably lithium C₁-C₄-alkoxide and most preferably lithium C₁-C₂-alkoxide; potassium C₁-C₆-alkoxide, preferably potassium C₁-C₄-alkoxide and most preferably potassium C₁-C₂-alkoxide, and mixtures thereof, together with the protonated form of Z as defined above. Preferably, the base is selected from the group comprising sodium hydroxide and sodium C₁-C₆-alkoxide, preferably sodium C₁-C₄-alkoxide and most preferably sodium C₁-C₂-alkoxide, and mixtures thereof. In one embodiment, the base is sodium hydroxide and/or sodium C₁-alkoxide. For example, the base is sodium hydroxide and sodium C₁-alkoxide, i.e. a mixture of sodium hydroxide and sodium C₁-alkoxide. Alternatively, the base is sodium hydroxide or sodium C₁-alkoxide, preferably sodium hydroxide. The combination of a base with the protonated form of Z is especially preferred if Z in general formula I is NHR₉ or NR₁₀R₁₁ with R₉, R₁₀ and R₁₁ being independently selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryl, C₇-C₁₅-arylalkyl, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, C₉-C₁₅-alkenylarylalkyl; or R₁₀ and R₁₁ form a C₃-C₉-alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O.

[0133] The base can be added as such to the process. Alternatively, the base is in form of an aqueous solution or the base is provided in an organic solvent, preferably the organic solvent is selected from the group comprising methanol, ethanol, n-propanol, tert.-butanol, dichloromethane, tetrachloroethylene, tetrahydrofuran, ethyl acetate, acetone, N,N-dimethylformamide, dimethyl sulfoxide, dioxane, such as 1,3-dioxane or 1,4-dioxane, 1,2-dimethoxyethane, diethyleneglycol dimethyl ether, triethyleneglycol dimethyl ether and mixtures thereof. Preferably, the base is provided in an organic solvent, preferably the organic solvent is tetrachloroethylene.

[0134] The process of the present invention can be carried out over a wide temperature range. However, it is preferred that the process is carried out at elevated temperature. For example, the process is carried out at a temperature of at

least 30 °C, preferably in the range from 30 to 120 °C, more preferably in the range from 40 to 100 °C, and most preferably in the range from 40 to 90 °C.

[0135] It is further appreciated that the process can be carried out in an organic solvent. Preferably the organic solvent is selected from the group comprising methanol, ethanol, n-propanol, tert.-butanol, dichloromethane, tetrachloroethylene, tetrahydrofuran, ethyl acetate, acetone, N,N-dimethylformamide, dimethyl sulfoxide, dioxane, such as 1,3-dioxane or 1,4-dioxane, 1,2-dimethoxyethane, diethyleneglycol dimethyl ether, triethyleneglycol dimethyl ether and mixtures thereof.

[0136] If the base is provided in an organic solvent, the organic solvent is preferably the same as used in the process.

[0137] It is a further requirement of the present invention that the process is carried out under phase-transfer conditions. Such phase-transfer conditions are well known in the art such that the skilled person will easily apply reaction conditions that are suitable for the reaction mentioned. The skilled person can also apply variants of such reactions which are known per se and are not mentioned herein in detail.

[0138] In particular, the contacting of the compound of formula II is carried out in the presence of a phase-transfer catalyst with the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene, and a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof, or a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof together with the protonated form of Z as defined above.

[0139] The phase-transfer catalyst can be selected from any phase-transfer catalyst known in the art. However, the phase-transfer catalyst is preferably selected from a quaternary ammonium salt, tetraalkylphosphonium chloride, tetraalkylphosphonium bromide and mixtures thereof. More preferably, the phase-transfer catalyst is a tetraalkylammonium salt or a trialkylarylammonium salt, and most preferably the phase-transfer catalyst is selected from the group comprising benzyltrimethylammonium hydroxide, benzyltriethylammonium chloride, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium hydrogensulfate, tetrabutylammonium hydroxide, methyltriocetyl ammonium chloride, cetyl pyridinium and mixtures thereof.

[0140] Such phase-transfer catalysts are well known in the art such that the skilled person will easily apply catalysts that are suitable for the reaction mentioned. The skilled person can also apply variants of such catalysts which are known per se and are not mentioned herein in detail.

[0141] The amount of phase-transfer catalysts can be chosen as desired within wide limits, preferably being 0.1 to 100 wt.-%, based on the weight of the ketone of the general formula II.

[0142] One advantage of the present process is that the process can be carried out in a one-pot process, and thus avoids elaborate purification steps for obtaining the desired α -functionalized ketones. The yield and purity of the desired α -functionalized ketones are thus significantly increased.

[0143] The term "one-pot process" in the meaning of the present invention refers to a process that can be carried out without the isolation and purification of intermediate products.

[0144] It is thus appreciated that the α -functionalized ketone is obtained in a one-pot reaction.

[0145] It has been found that the sequence of addition of the reagents is important for the success of the reaction. The best yields are obtained when the ketone of the general formula II, the phase-transfer catalyst, the base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof, or the base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof together with the protonated form of Z as defined above and, if present, the organic solvent are contacted first and the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is metered in.

[0146] The reaction and contacting are carried out by mixing the components, i.e. the ketone of the general formula II, the phase-transfer catalyst, the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene, and the base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof, or the base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof together with the protonated form of Z as defined above. The skilled person will adapt the mixing conditions (such as the configuration of mixing tools and mixing speed) according to his process equipment.

[0147] The process of the present invention may comprise further steps for isolating and/or purifying the obtained α -functionalized ketones of general formula I.

[0148] For example, the process may further comprise a step of

- i) separating the obtained organic and aqueous phases, and/or
- ii) extracting the obtained aqueous phase with the organic solvent used in the process and combining the obtained organic phases, and/or
- iii) acidifying the obtained organic phase to a pH of 3 to 6.5.

[0149] In one embodiment, the process further comprises the steps of

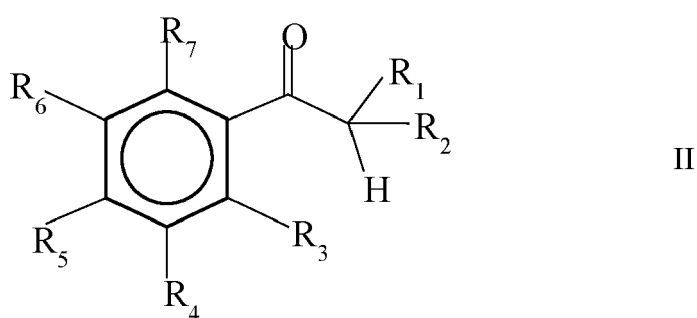
- i) separating the obtained organic and aqueous phases, and
- ii) extracting the obtained aqueous phase with the organic solvent used in the process and combining the obtained organic phases, and
- iii) acidifying the obtained organic phase to a pH of 3 to 6.5.

[0150] Additionally, the process may further comprise a step of drying the obtained α -functionalized ketones of general formula I.

[0151] The ketone of the general formula II used can be easily α -functionalized in high yields and purity. The residue from work-up, which consists mainly of organic solvent and (unchanged) phase-transfer catalyst, can be reused e.g. in the process as solvent and (re-halogenated) phase-transfer catalyst.

[0152] According to another aspect, an α -functionalized ketone obtained by the process as defined herein, is provided.

[0153] Thus, the α -functionalized ketone of is obtained by a process comprising the contacting of a ketone of the general formula II



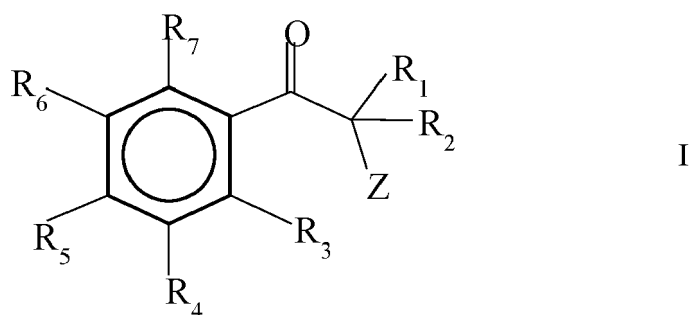
wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and R_7 are as defined above, under phase-transfer conditions with an at least partially halogenated C_2 - C_8 -alkane and/or C_2 - C_8 -alkene, and a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C_1 - C_8 -alkoxide, earth alkali metal C_1 - C_8 -alkoxide and mixtures thereof, or a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C_1 - C_8 -alkoxide, earth alkali metal C_1 - C_8 -alkoxide and mixtures thereof together with the protonated form of Z as defined above.

[0154] With regard to the definition of the α -functionalized ketone, the ketone of the general formula II, the R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and R_7 and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the process and the α -functionalized ketone of the general formula I obtained by the process of the present invention.

[0155] The inventors surprisingly found that the process allows the preparation of α -functionalized ketones that have not been accessible by the processes of the prior art up to now and thus also results in new α -functionalized ketones that can be used as photoinitiator.

[0156] In another aspect, the present specification thus refers to an α -functionalized ketone as defined herein, with the proviso that at least one of R_3 , R_4 , R_5 , R_6 and R_7 is linear or branched C_2 - C_8 -alkenyl, preferably C_2 - C_6 -alkenyl and most preferably C_2 - C_3 -alkenyl, C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy, and C_9 - C_{15} -alkenylarylalkoxy, preferably C_9 - C_{12} -alkenylarylalkoxy and most preferably C_9 - C_{10} -alkenylarylalkoxy. The α -functionalized ketone is preferably obtained by the process of the present invention.

[0157] The new α -functionalized ketone is thus preferably an α -functionalized ketone of the general formula I,

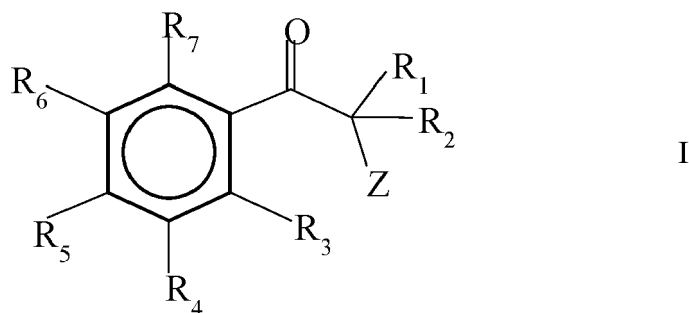


wherein R_1 and R_2 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, linear or branched C_2 - C_8 -alkenyl, C_5 - C_8 -cycloalkenyl, linear or branched C_2 - C_8 -alkynyl, C_6 - C_{14} -aryl or form C_3 - C_{12} -cycloalkyl or C_5 - C_{12} -cycloalkenyl together with the connecting C atom; R_3 , R_4 , R_5 , R_6 and R_7 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_6 - C_{14} -aryl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy, $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_6 - C_{14} -aryl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, or two adjacent R form an aromatic system together with the benzene ring of formula I; Z is selected from OR_9 , NHR_9 and $NR_{10}R_{11}$ with R_9 , R_{10} and R_{11} being independently selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_6 - C_{14} -aryl, C_7 - C_{15} -arylalkyl, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy, C_9 - C_{15} -alkenylarylalkyl; or R_{10} and R_{11} form a C_3 - C_9 -alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O; with the proviso that at least one of R_3 , R_4 , R_5 , R_6 and R_7 is linear or branched C_2 - C_8 -alkenyl, e.g. linear C_2 - C_8 -alkenyl, preferably linear or branched C_2 - C_6 -alkenyl, e.g. linear C_2 - C_6 -alkenyl, and most preferably C_2 - C_3 -alkenyl, C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy, and C_9 - C_{15} -alkenylarylalkoxy, preferably C_9 - C_{12} -alkenylarylalkoxy and most preferably C_9 - C_{10} -alkenylarylalkoxy.

[0158] With regard to the definition of the α -functionalized ketone, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and Z and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the process and the α -functionalized ketone of the general formula I obtained by the process of the present invention.

[0159] A further aspect thus refers to the use of the new α -functionalized ketone as photoinitiator.

[0160] More precisely, the present specification also relates to the use of an α -functionalized ketone of the general formula I as photoinitiator,



wherein R_1 and R_2 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, linear or branched C_2 - C_8 -alkenyl, C_5 - C_8 -cycloalkenyl, linear or branched C_2 - C_8 -alkynyl, C_6 - C_{14} -aryl or form C_3 - C_{12} -cycloalkyl or C_5 - C_{12} -cycloalkenyl together with the connecting C atom; R_3 , R_4 , R_5 , R_6 and R_7 are the same or different and are independently selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_6 - C_{14} -aryl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy, $N(R_8)_2$ or SR_8 with R_8 being selected from linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_6 - C_{14} -aryl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy or R_8 form a C_3 - C_9 -alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, or two adjacent R form an aromatic system together with the benzene ring of formula I; Z is selected from OR_9 , NHR_9 and $NR_{10}R_{11}$ with R_9 , R_{10} and R_{11} being independently selected from H, linear or branched C_1 - C_8 -alkyl, linear or branched C_2 - C_8 -alkenyl, C_1 - C_8 -alkoxy, C_2 - C_8 -alkenyloxy, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkoxy, C_6 - C_{14} -aryl, C_7 - C_{15} -arylalkyl, C_7 - C_{15} -arylalkoxy, C_9 - C_{15} -alkenylarylalkoxy, C_9 - C_{15} -alkenylarylalkyl; or R_{10} and R_{11} form a C_3 - C_9 -alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O; with the proviso that at least one of R_3 , R_4 , R_5 , R_6 and R_7 is linear or branched C_2 - C_8 -alkenyl, e.g. linear C_2 - C_8 -alkenyl, preferably linear or branched C_2 - C_6 -alkenyl, e.g. linear C_2 - C_6 -alkenyl, and most preferably C_2 - C_3 -alkenyl, C_2 - C_8 -alkenyloxy, preferably C_2 - C_6 -alkenyloxy and most preferably C_3 - C_5 -alkenyloxy, and C_9 - C_{15} -alkenylarylalkoxy, preferably C_9 - C_{12} -alkenylarylalkoxy and most preferably C_9 - C_{10} -alkenylarylalkoxy.

[0161] With regard to the definition of the α -functionalized ketone, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and Z and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the process and the α -functionalized ketone of the general formula I obtained by the process of the present invention.

[0162] A further aspect refers to a photopolymerizable composition comprising the α -functionalized ketone as defined herein and at least one photopolymerizable unsaturated compound.

[0163] It is appreciated that any photopolymerizable unsaturated compound that is typically used in the articles to be prepared and is well known can be used as the at least one photopolymerizable unsaturated compound. For example, the at least one photopolymerizable unsaturated compound can be a compound as described in WO 2004/099262 A1.

[0164] The photopolymerizable composition may also contain optional additives and/or optional further photoinitiators and/or coinitiator. The optional additives and/or photoinitiators and/or coinitiator are not limited any include any additive and/or photoinitiators and/or coinitiator typically used in the articles to be prepared and are well known in the art. For example, the additives and/or photoinitiators and/or coinitiator can be one or more compounds described as additives (C) and/or photoinitiators and/or coinitiator (D) in WO 2004/099262 A1.

[0165] A further aspect thus refers to the use of the photopolymerizable composition comprising the α -functionalized ketone and at least one photopolymerizable unsaturated compound, as defined herein, as photoinitiator.

[0166] It is preferred that the α -functionalized ketone of the general formula I or the photopolymerizable composition comprising the α -functionalized ketone and at least one photopolymerizable unsaturated compound as defined herein is used as photoinitiator in a method of preparing an article.

[0167] Thus, the α -functionalized ketone of the general formula I or the photopolymerizable composition comprising the α -functionalized ketone and at least one photopolymerizable unsaturated compound as defined herein is preferably used as photoinitiator in an article, preferably a packaging article, more preferably a food or beverage packaging article, an article of flooring or an article of furniture.

[0168] With regard to the definition of the α -functionalized ketone, the photopolymerizable composition and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the process and the α -functionalized ketone of the general formula I obtained by the process of the present invention.

[0169] In view of the advantages obtained, the present specification refers in another aspect to a method of preparing an article. The method comprising the steps of

- a) preparing a coating and/or ink composition comprising the α -functionalized ketone as defined herein or the photopolymerizable composition comprising an α -functionalized ketone as defined herein,
- b) applying the coating and/or ink composition at least partially on at least one surface of an article, and
- c) curing the coating and/or ink composition by means of ultra-violet radiation.

[0170] With regard to the definition of the α -functionalized ketone, the photopolymerizable composition and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the process and the α -functionalized ketone of the general formula I obtained by the process of the present invention.

[0171] It is appreciated that coating and/or ink compositions are well known to the skilled person and do not need to be described in more detail in the present application. Thus, any coating and/or ink composition that is typically used for the articles to be prepared and is well known can be used. The person skilled in the art will adapt the coating and/or ink composition according to the article to be prepared and/or his process equipment.

[0172] Furthermore, any suitable application means known in the art may be used for carrying out application step b). However, application step b) is preferably carried out by brushing, dripping, printing, spraying, dipping and the like. Most preferably, application step b) takes place by spraying.

[0173] Any suitable curing means using ultra-violet radiation known in the art may be used for carrying out curing step c). Such curing steps are well known in the art and the skilled person will adapt the curing conditions according to his process equipment and the article to be prepared.

[0174] In view of the above, the present specification refers in another aspect to an article obtained by a method of preparing an article, as defined herein.

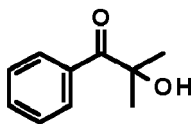
[0175] It is preferred that the article is a packaging article, an article of flooring or an article of furniture. If the article is a packaging article, the article is preferably a food or beverage packaging article. If the article is an article of flooring, the article is preferably a tile, most preferably a ceramic, vinyl or composite tile, or a floorboard, most preferably a wooden or composite floorboard.

[0176] The scope and interest of the invention will be better understood based on the following examples which are intended to illustrate certain embodiments of the invention and are non-limitative.

EXAMPLES

Example 1: Preparation of 2-hydroxy-2-methyl-1-phenyl-1-propanone

[0177]



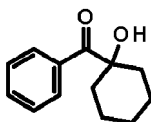
[0178] A 500 mL double-walled-jacket, multi-necked flask, fitted with a mechanical stirrer, reflux condenser, connected to a thermostat, thermometer and a dropping funnel, is charged with 59.3 g (400 mmol) isobutyrophenone, 2.58 g (8 mmol) tetrabutylammonium bromide and 373.3 g (2.80 mol) 30% aqueous sodium hydroxide solution. This is heated with stirring to 82-85 °C, and within 90 minutes a solution of 94.7 g (408 mmol) hexachloroethane in 199 g tetrachloroethylene is added. The reaction mixture is stirred for another 3 hours at 84 °C. The temperature is then lowered to 60 °C and left unstirred for phase separation. The lower organic phase is split off; the aqueous phase is extracted with 50 g tetrachloroethylene, the organic phases are combined and 100 g water added. pH is then adjusted to 6.0 using 5% acetic acid. The organic phase is split off and distilled in vacuo.

[0179] Yield: 56.8 g (86.5%) 2-Hydroxy-2-methyl-1-phenyl-1-propanone as a pale yellow oil; b.p. 96 °C, 1 mbar, 99% purity (GC). NMR data are identical with the data of an authentic reference sample.

[0180] Tetrachloroethylene (b.p. 55 °C, 200 mbar) is nearly quantitatively recovered (94%, 99.6% purity).

Example 2: Preparation of (1-hydroxycyclohexyl) phenyl ketone

[0181]



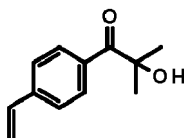
[0182] A 500 mL double-walled-jacket multi-necked flask, fitted with a mechanical stirrer, reflux condenser, thermometer and a dropping funnel connected to a thermostat, is charged with 75.3 g (400 mmol) cyclohexyl phenyl ketone, 2.58 g (8 mmol) tetrabutylammonium bromide and 373.3 g (2.80 mol) 30% aqueous sodium hydroxide solution. This is heated with stirring to 82-85 °C and within 90 minutes a solution of 96.6 g (408 mmol) hexachloroethane in 199 g tetrachloroethylene is added. The reaction mixture is stirred for another 3 hours at 84 °C. The temperature is then lowered to 60 °C and left unstirred for phase separation. The lower organic phase is split off; the aqueous phase is extracted with 50 g tetrachloroethylene, the organic phases are combined and 100 g water added. pH is then adjusted to 6.0 using 5% acetic acid. The organic phase is split off and the product is vacuum distilled.

[0183] Yield: 66.3 g (81.2%) (1-hydroxycyclohexyl) phenyl ketone (Irgacure 184) as a pale yellow oil; b.p. 143 °C, 0.7 mbar, 95% purity (GC). NMR data are identical with the data of an authentic reference sample.

[0184] Tetrachloroethylene (b.p. 55 °C, 200 mbar) is nearly quantitatively recovered (97%, 99.5% purity).

Example 3: Preparation of 2-hydroxy-2-methyl-1-(4-vinylphenyl)propan-1-one

[0185]

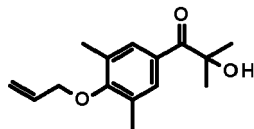


[0186] To a multi-necked, double-walled-jacket 500 mL flask, fitted with a thermometer, reflux condenser and a mechanical stirrer was charged 4-vinylisobutyrophenone (1.20 g, 6.89 mmol), tetrabutylammonium bromide (44 mg, 0.14 mmol), sodium hydroxide solution 30% (6.5 g, 48.8 mmol), tetrachloroethylene (6 g) and ProStab (1% solution in toluene, 0.02 g). The mixture was heated to 50 °C with stirring and a solution of hexachloroethane (2.19 g, 9.25 mmol) in tetrachloroethylene (5 g) is added dropwise within 30 minutes time. Stirring is continued overnight at 50 °C, the reaction mixture cooled to ambient temperature and extracted with tetrachloroethylene (3 x 10 mL). The organic phase is acidified to pH 4 with 5% acetic acid, washed with water (3 x 10 mL) and dried with sodium sulfate. The solvent is evaporated to give the product [1.12 g, 5.89 mmol, 86%] as a pale yellow oil.

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.61 (s, 6 H), 4.16 (br. s, 1 H), 5.40 (dd, 1 H), 5.87 (dd, 1 H), 6.74 (dd, 1 H), 7.44-7.48 (m, 2 H), 7.98-8.02 ppm (m, 2 H).

Example 4: Preparation of 1-(4-allyloxy-3,5-dimethyl-phenyl)-2-hydroxy-2-methyl-propan-1-one

[0187]

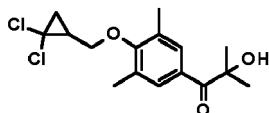


[0188] To a reaction flask containing 100 ml of benzene and the solution of NaOH (40 g, 1 mol) in 40 ml of water is added tetrabutylammonium bromide (2 g), 1-(4-allyloxy-3,5-dimethyl-phenyl)-2-methyl-propan-1-one (19.15 g, 0.082 mol, prepared as described below) and hexachloroethane (39 g, 0.165 mol). The heterogeneous mixture is vigorously stirred under nitrogen during 90 minutes at 60°C. The mixture is then cooled to room temperature and diluted with 300 ml of water and 250 ml of *t*-butyl-methyl ether. The organic phase is separated and the aqueous phase is extracted with 200 ml of *t*-butyl-methyl ether. The combined organic phases are dried over magnesium sulfate and evaporated. The semisolid product (34 g) is chromatographed on silica gel with hexane-ethyl acetate (4:1) to afford 18.69 g of the title product as a light yellow oil.

¹H-NMR (CDCl₃, 400 MHz, δ ppm): 7.73 (s, 2ArH), 6.15-6.07 (m, 1H), 5.48-5.47 (dd, 1H), 5.44-5.42 (dd, 1H), 4.38-4.36 (d, 2H, CH₂), 4.22 (s, 1H, OH), 2.34 (s, 2xCH₃), 1.64 (s, 2xCH₃)

Example 5 (Comparative example to example 4): Preparation of 1-(4-allyloxy-3,5-dimethyl-phenyl)-2-hydroxy-2-methyl-propan-1-one using tetrachloromethane

[0189] Running the reaction described in example 4 under same conditions, but replacing hexachloroethane with tetrachloromethane, leads to the formation of a considerable amount (-10%) of the side-product 1-[4-[(2,2-dichlorocyclopropyl)-methoxy]-3,5-dimethyl-phenyl]-2-hydroxy-2-methyl-propan-1-one.



[0190] Analytical data for 1-[4-[(2,2-dichlorocyclopropyl)-methoxy]-3,5-dimethyl-phenyl]-2-hydroxy-2-methyl-propan-1-one:

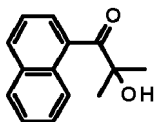
Colorless oil

MS for C₁₆H₂₀Cl₂O₃ (331.23); found M = 331.

¹H-NMR (CDCl₃, 400 MHz, δ ppm): 7.72 (s, 2 ArH), 4.20 (s, 1H, OH), 4.06-3.91 (m, 2H, CH₂-O), 2.36 (s, 2xCH₃), 2.19-2.11 (m, 1H), 1.77-1.72 (m, 1H), 1.61 (s, 2xCH₃), 1.35-1.25 (s, 1H).

Example 6: Preparation of 2-hydroxy-2-methyl-1-(1-naphthyl)propan-1-one

[0191]



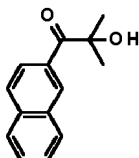
[0192] Using the same equipment as in examples 1-5, to a mixture of 1-isobutyronaphthone (1.40 g, 7.06 mmol), tetrabutylammonium bromide (46 mg, 0.14 mmol), sodium hydroxide solution 30% (6.6 g, 49.5 mmol) and tetrachloroethylene (5 g) is added hexachloroethane (1.84 g, 7.77 mmol) dissolved in tetrachloroethylene (4 g). This mixture is stirred at 50 °C for 4.5 h. After cooling to room temperature, acetic acid 5% is added to adjust pH to 4 and the organic phase is washed with water (3 x 10 mL). The organic phase is dried over sodium sulfate and the evaporated to dryness.

The crude product is purified by column chromatography [$c\text{-C}_6\text{H}_{12}/\text{AcOEt}$, 4:1 v:v] and the title compound is isolated as a pale yellow oil [0.95 g, 4.43 mmol, 63%].

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3): δ = 1.52 (s, 6 H), 3.87 (s, 1 H), 7.43 (dd, 1 H), 7.47-7.53 (m, 2 H), 7.56 (dd, 1 H), 7.73-7.79 (m, 1 H), 7.82-7.87 (m, 1 H), 7.88-7.91 ppm (m, 1 H)

Example 7: Preparation of 2-hydroxy-2-methyl-1-(2-naphthyl)propan-1-one

[0193]

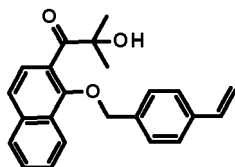


[0194] A 25 mL three-necked flask is charged 2-isobutyronaphthone (0.50 g, 2.52 mmol), tetrabutylammoniumbromide (16 mg, 0.05 mmol), sodium hydroxide solution (30%, 2.35 g, 17.65 mmol) and tetrachloroethylene (10 g). To this is added hexachloroethane (0.66 g, 2.77 mmol), dissolved in tetrachloroethylene (2.5 g) and the reaction mixture is stirred at 50 °C overnight. After cooling to room temperature, pH is adjusted to 4 with 5% acetic acid and the organic phase washed with water (3 x 10 mL). The organic phase is dried over sodium sulfate and the solution evaporated to dryness. The crude product is purified by column chromatography on silicagel [$c\text{-C}_6\text{H}_{12}/\text{AcOEt}$, 9:1 v:v], providing the title compound as a yellowish oil.

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3): δ = 1.71 (s, 6 H), 4.16 (s, 1 H), 7.53-7.63 (m, 2 H), 7.85-7.89 (m, 2 H), 7.95 (dd, 1 H), 8.05 (dd, 1 H), 8.60 (d, 1 H)

Example 8: Preparation of 2-hydroxy-2-methyl-1-[1-[(4-vinylphenyl)methoxy]-2-naphthyl]propan-1-one

[0195]

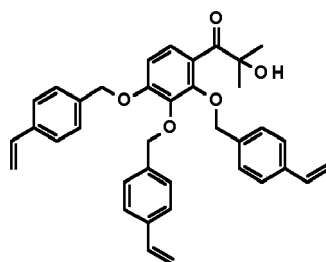


[0196] To a mixture of 2-methyl-1-[1-[(4-vinylphenyl)methoxy]-2-naphthyl]propan-1-one (0.40 g, 1.21 mmol), tetrabutylammonium bromide (8 mg, 0.02 mmol), sodium hydroxide solution (30%, 1.13 g, 8.47 mmol) and tetrachloroethylene (3.5 g) is added a solution of hexachloroethane (0.32 g, 1.33 mmol) in tetrachloroethylene (1 g) at 50 °C. Stirring is continued for 4 h at 50 °C. After cooling to room temperature, the organic phase is split off and the aqueous phase is extracted with tetrachloroethylene (3 x 10 mL). After pH of the organic phase is adjusted to 4 (5% acetic acid), the organic phase is washed with water (3 x 10 mL), dried over sodium sulfate and evaporated to dryness. The crude product is subjected to column chromatography [$c\text{-C}_6\text{H}_{12}/\text{AcOEt}$, 19:1 v:v] to give the title compound [0.42 g, 1.96 mmol, 78%] as a slightly yellow oil.

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3): δ = 1.45 (s, 6 H), 3.96 (s, 1 H), 5.04 (s, 2 H), 5.27 (dd, 1 H), 5.77 (dd, 1 H), 6.73 (dd, 1 H), 7.31 (d, 1 H), 7.40-7.47 (m, 4 H), 7.51-7.57 (m, 2 H), 7.67 (d, 1 H), 7.84-7.90 (m, 1 H), 8.11-8.16 ppm (m, 1H); $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): δ = 27.2, 78.3, 114.4, 122.5, 124.0, 124.7, 126.6, 127.0, 127.5, 127.7, 128.3, 128.9, 130.8, 135.7, 135.9, 136.4, 137.9, 151.7, 212.0 ppm

Example 9: Preparation of 2-hydroxy-2-methyl-1-[2,3,4-tris[(4-vinylphenyl)methoxy]-phenyl]propan-1-one

[0197]



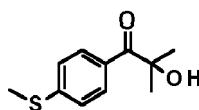
[0198] To a 25 mL three-necked flask is charged 2-methyl-1-[2,3,4-tris[(4-vinylphenyl)methoxy]phenyl]propan-1-one (250 mg, 0.46 mmol), tetrabutylammonium bromide (3 mg, 0.01 mmol), sodium hydroxide solution (30%, 0.43 g, 3.22 mmol) and tetrachloroethylene (2.5 g). To this is added a solution of hexachloroethane (120 mg, 0.50 mmol) in tetrachloroethylene (0.8 g). The reaction mixture is stirred at 50 °C overnight. The reaction mixture is allowed to come to room temperature and extracted with tetrachloroethylene (3 x 10 mL), the organic phase pH-adjusted to 4, washed with water (3 x 10 mL), dried over sodium sulfate and evaporated to dryness. The residue is chromatographed on silicagel [heptanes/AcOEt, 4:1 v:v] giving the title compound [220 mg, 0.39 mmol, 86%] as a pale yellow oil.

IGM

B 15265-EP ¹H-NMR (400.1 MHz, CDCl₃): δ = 1.35 (s, 6 H), 3.99 (s, 1 H), 5.04-5.10 (3 x s, 3 x 2 H), 5.22-5.30 (3 x dd superimposed, 3 x 1 H), 5.71-5.79 (3 x dd superimposed, 3 x 1 H), 6.65-6.78 (3 x dd superimposed, 3 x 1 H), superimposed with 6.76 (d, 1 H), 6.98 (d, 1 H), 7.20-7.44 ppm (m, 12 H); ¹³C-NMR (100.6 MHz, CDCl₃): δ = 27.3, 70.9, 75.4, 76.7, 78.0, 109.6, 123.3, 126.3, 126.4, 126.5, 127.3, 127.8, 128.9, 129.0, 135.8, 136.0, 136.4, 136.5, 136.6, 137.6, 137.7, 141.4, 150.0, 155.1, 210.4 ppm

Example 10: Preparation of 2-hydroxy-2-methyl-1-(4-methylthiophenyl)propan-1-one

[0199]

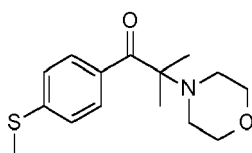


[0200] Sodium hydroxide solution (w=50%, 12.35 g, 154.4 mmol) and tetrabutylammonium bromide (0.15 g, 0.46 mmol) were added to a solution of 2-methyl-1-(4-methylthiophenyl)-propan-1-one (3.00 g, 15.4 mmol) and hexachloroethane (5.48 g, 23.16 mmol) in tetrachloroethylene (8 mL). The reaction mixture was stirred at 50°C for four hours. The resulting solution was taken up with water (20 mL) and the phases were separated. The pH of the aqueous layer was adjusted to 3 with diluted HCl solution. Afterwards, it was extracted with tetrachloroethylene (3 x 50 mL). The combined organic phases were washed with brine (50 mL), dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was obtained as a yellow oil (2.96 g, 14.1 mmol, 91% yield).

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.64 (s, 6H), 2.54 (s, 3H), 4.12 (wide s, 1H), 7.26-7.32 (m, 2H), 7.96-8.02 (m, 2 H) ppm. ¹³C-NMR (100.6 MHz, CDCl₃): δ = 14.7, 28.6, 76.1, 124.79, 129.4, 130.3, 146.3 ppm.

Reference Example 11: Preparation of 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propan-1-one

[0201]



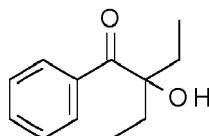
[0202] A mixture of sodium methoxide (30% in methanol, 5.56 g, 30.9 mmol), methanol (5), 2-methyl-1-(4-methylthiophenyl)propan-1-one (1.00 g, 5.14 mmol) and hexachloroethane (1.34 g, 5.66 mmol) was stirred at room temperature for 2 d. Then, methanol was removed from the reaction mixture by distillation under reduced pressure and morpholine (22.4 g, 257 mmol) and sodium hydroxide solution (50%, 4.12 g, 51.5 mmol) were added. The reaction mixture was stirred under reflux for 10 h. Then, the reaction mixture was cooled down to room temperature, the solvent evaporated

under reduced pressure and the residue taken up with water (30 mL). The phases were separated and pH of the aqueous layer was adjusted to 1.0 with hydrochloric acid solution (1M). The aqueous layer was extracted with tert-butylmethylether (3 x 50 mL) to remove impurities. Then the pH of the aqueous layer was adjusted to 14.0 with sodium hydroxide solution (50%) and extracted again with tert-butylmethylether (3 x 50 mL). The combined organic layers of the second extraction were washed with brine (50 mL), dried over Na₂SO₄ and the solvent was removed under vacuum. The crude product of 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propan-1-one was obtained as slightly yellowish crystals, (0.91 g, 3.3 mmol, 63 % yield).

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.31 (s, 6H), 2.53 (s, 3H), 2.55-2.61 (m, 4H), 3.66-3.73 (m, 4H), 7.20-7.26 (m, 2H), 8.49-8.54 (m, 2 H) ppm. ¹³C-NMR (100.6 MHz, CDCl₃): δ = 14.4, 20.4, 47.2, 67.3, 68.3, 124.3, 130.3, 131.8, 144.9, 201.9 ppm. Melting point: 66-68 °C

Example 12: Preparation of 2-ethyl-2-hydroxy-1-phenyl-butan-1-one

[0203]

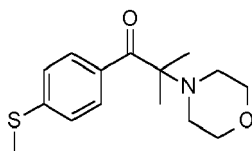


[0204] Sodium hydroxide solution (w=50%, 9.08 g, 113 mmol) and tetrabutylammonium hydrogensulfate (0.19 g, 0.57 mmol) were added to a solution of 2-ethyl-1-phenyl-butan-1-one (2.00 g, 11.4 mmol) and hexachloroethane (2.96 g, 12.48 mmol) in tetrachloroethylene (12 mL). The reaction mixture was stirred at 50°C for 1.5 d. The resulting solution was taken up with water (20 mL) and the phases were separated. The pH of the aqueous layer was adjusted to 3 with dilute HCl solution (1M), and extracted with tetrachloroethylene (3 x 50 mL). The combined organic phases were washed with brine (50 mL), dried over sodium sulfate and the solvent was removed under reduced pressure. 2-Ethyl-2-hydroxy-1-phenyl-butan-1-one was obtained as a colorless oil (2.09 g, 10.9 mmol, 96% yield).

¹H-NMR (400.1 MHz, CDCl₃): δ = 0.82-0.86 (t, 6H), 1.92-2.04 (m, 2H), 2.06-2.18 (m, 2H), 4.39 (s, 1H), 7.45-7.54 (m, 2H), 7.58-7.65 (m, 1H), 7.97-8.05 (m, 2H) ppm.

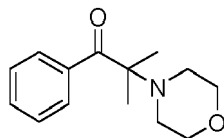
Example 13: Preparation of 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propan-1-one

[0205]



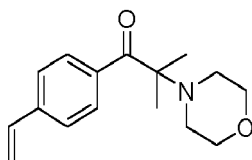
[0206] A mixture of sodium methoxide (30% in methanol, 5.56 g, 30.9 mmol), methanol (5), 2-methyl-1-(4-methylthiophenyl)propan-1-one (1.00 g, 5.14 mmol) and hexachloroethane (1.34 g, 5.66 mmol) was stirred at 40°C for 24 h. Then, morpholine (22.4 g, 257 mmol) was added and methanol was removed from the reaction mixture by distillation. Afterwards, sodium hydroxide solution (50%, 4.12 g, 51.5 mmol) and tetrabutylammonium hydrogensulfate (0.09 g, 0.27 mmol) were added and the reaction mixture was stirred under reflux for 10 h. Then, the reaction mixture was cooled down to room temperature, the solvent was evaporated under reduced pressure and the residue was taken up with water (30 mL). The phases were separated and the pH of the aqueous layer was adjusted to 7 with saturated ammonium chloride solution. The aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄ and the solvent was evaporated. The crude product was purified by preparative thin layer chromatography on silica gel [cyclohexane/ethyl acetate, 5:1 v:v]. 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propan-1-one was obtained as a colorless oil (0.95 g, 3.2 mmol, 61 % yield).

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.31 (s, 6H), 2.53 (s, 3H), 2.55-2.61 (m, 4H), 3.66-3.73 (m, 4H), 7.20-7.26 (m, 2H), 8.49-8.54 (m, 2 H) ppm. ¹³C-NMR (100.6 MHz, CDCl₃): δ = 14.4, 20.4, 47.2, 67.3, 68.3, 124.3, 130.3, 131.8, 144.9, 201.9 ppm.

Reference Example 14: Preparation of 2-methyl-2-morpholino-1-phenylpropan-1-one**[0207]**

[0208] A mixture of sodium methoxide (30% in methanol, 22.1 g, 0.410 mol), methanol (30 mL), isobutyrophenone (10.12 g, 68.28 mmol) and hexachloroethane (32.33 g, 136.6 mmol) was stirred at 40 °C for 2 d. Then, further sodium methoxide (30% in methanol, 11.85 g, 0.221 mol) and another equivalent of hexachloroethane (16.2 g, 68.3 mmol) was added and the reaction mixture was stirred at 50 °C for 6 h. Afterwards, methanol was removed from the reaction mixture by distillation under reduced pressure and morpholine (150 g, 1.72 mol) and sodium hydroxide solution (50%, 54.6 g, 0.683 mol) were added. The reaction mixture was stirred overnight at 110°C. Then, it was cooled down to room temperature and slowly poured into conc. hydrochloric acid solution (500 mL). The aqueous layer was separated, the pH was adjusted to 0 by adding further conc. hydrochloric acid solution and then it was extracted with tert-butylmethylether (3 x 200 mL) to remove impurities. Then, the pH of the aqueous layer was adjusted to 14 with sodium hydroxide solution (50%) and extracted again with tert-butylmethylether (3 x 200 mL). The combined organic layers of the second extraction were washed with brine (2 x 100 mL), dried over Na₂SO₄ and the solvent was evaporated. The crude product of 2-methyl-2-morpholino-1-phenylpropan-1-one was obtained as red crystals, (7.60 g, 32.6 mmol, 48 % yield).

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.34 (s, 6H), 2.57-2.63 (m, 4H), 3.68-3.76 (m, 4H), 7.40-7.46 (m, 2H), 7.50-7.54 (m, 1H), 8.53-8.58 (m, 2H) ppm. ¹³C-NMR (100.6 MHz, CDCl₃): δ = 20.3, 47.1, 67.4, 68.4, 124.9, 130.3, 132.4, 135.9, 203.3 ppm. Melting point: 79-81 °C

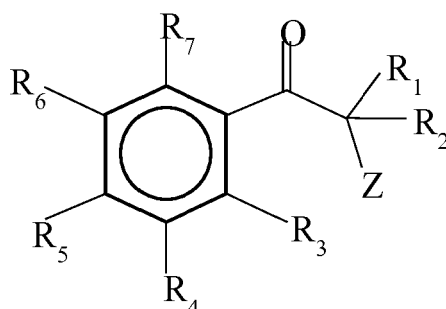
Reference Example 15: Preparation of 2-methyl-2-morpholino-1-(4-vinylphenyl)propan-1-one**[0209]**

[0210] A mixture of sodium methoxide (30% in methanol, 3.72 g, 68.9 mmol), methanol (5 mL), 2-methyl-1-(4-vinylphenyl)propan-1-one (2.00 g, 11.5 mmol) and hexachloroethane (5.45 g, 23.0 mmol) was stirred at 40 °C for 2 d. Then, further sodium methoxide (30% in methanol, 1.85 g, 34.2 mmol) and another equivalent of hexachloroethane (2.75 g, 11.4 mmol) was added and the reaction mixture was stirred at 50 °C for 6 h. Afterwards, methanol was removed from the reaction mixture by distillation under reduced pressure and morpholine (25.0 g, 0.287 mol) and sodium hydroxide solution (50%, 9.18 g, 0.115 mol) were added. The reaction mixture was stirred overnight at 110°C. Then, it was cooled down to room temperature and slowly poured into conc. hydrochloric acid solution (50 mL). The aqueous layer was separated, the pH was adjusted to 0 by adding further conc. hydrochloric acid solution and then it was extracted with tert-butylmethylether (3 x 20 mL) to remove impurities. Then, the pH of the aqueous layer was adjusted to 14 with sodium hydroxide solution (50%) and extracted again with tert-butylmethylether (3 x 20 mL). The combined organic layers of the second extraction were washed with brine (2 x 10 mL), dried over Na₂SO₄ and the solvent was evaporated. The crude product was purified by preparative thin layer chromatography on silica gel (c- C₆H₁₂ : AcOEt = 2 : 1, v : v). 2-methyl-2-morpholino-1-(4-vinylphenyl)propan-1-one was obtained as a colorless oil, (1.78 g, 6.86 mmol, 60 % yield).

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.35 (s, 6H), 2.59-2.62 (m, 4H), 3.71-3.73 (m, 4H), 5.39 (dd, 1H), 5.89 (dd, 1H), 6.77 (dd, 1H) 7.42-7.50 (m, 2H), 8.51-8.58 (m, 2H) ppm. ¹³C-NMR (100.6 MHz, CDCl₃): δ = 20.2, 47.1, 67.4, 68.4, 116.3, 125.6, 130.7, 134.9, 136.1, 141.4, 202.6 ppm.

Claims

1. A process for the preparation of an α-functionalized ketone of the general formula I,



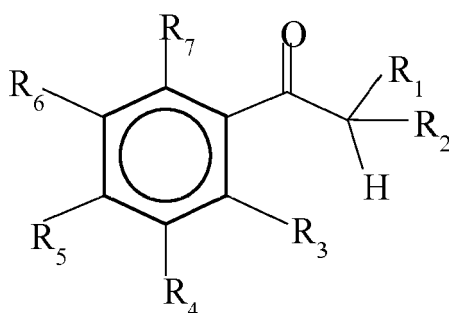
I

wherein R₁ and R₂ are the same or different and are independently selected from H, linear or branched C₁-C₈-alkyl, C₃-C₃-cycloalkyl, linear or branched C₂-C₈-alkenyl, C₅-C₈-cycloalkenyl, linear or branched C₂-C₈-alkynyl, C₆-C₁₄-aryl or form C₃-C₁₂-cycloalkyl or C₅-C₁₂-cycloalkenyl together with the connecting C atom;

R₃, R₄, R₅, R₆ and R₇ are the same or different and are independently selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₃-cycloalkyl, C₆-C₁₄-aryl, C₃-C₃-cycloalkoxy, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, N(R₈)₂ or SR₈ with R₈ being selected from linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₆-C₁₄-aryl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₃-cycloalkyl, C₃-C₃-cycloalkoxy, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, or two adjacent R form an aromatic system together with the benzene ring of formula I;

Z is selected from OR₉, NHR₉ and NR₁₀R₁₁ with R₉, R₁₀ and R₁₁ being independently selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkoxy, C₆-C₁₄-aryl, C₇-C₁₅-arylalkyl, C₇-C₁₅-arylalkoxy, C₉-C₁₅-alkenylarylalkoxy, C₉-C₁₅-alkenylarylalkyl; or R₁₀ and R₁₁ form a C₃-C₉-alicyclic system together with the connecting N or C atom, optionally one or more carbon atoms are replaced with O;

characterized in that a ketone of the general formula II



II

wherein R₁, R₂, R₃, R₄, R₅, R₆ and R₇ are as defined above, is contacted under phase-transfer conditions with an at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene, and

i) a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof,

or

ii) a base selected from the group comprising alkali metal hydroxide, earth alkali metal hydroxide, alkali metal C₁-C₈-alkoxide, earth alkali metal C₁-C₈-alkoxide and mixtures thereof together with the protonated form of Z as defined above.

2. The process according to claim 1, **characterized in that** R₁ and R₂ are the same.
3. The process according to claim 2, **characterized in that** R₁ and R₂ are selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl.
4. The process according to claim 1, **characterized in that** R₁ and R₂ are different and are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or

branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl.

5. The process according to claim 1, **characterized in that** R₁ and R₂ form C₄-C₁₀-cycloalkyl, preferably C₄-C₈-cycloalkyl, and most preferably C₆-cycloalkyl, together with the connecting C atom.
6. The process according to any one of claims 1 to 5, **characterized in that** R₃, R₄, R₅, R₆ and R₇ are the same.
7. The process according to claim 6, **characterized in that** R₃, R₄, R₅, R₆ and R₇ are selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl.
8. The process according to any one of claims 1 to 5, **characterized in that** R₃, R₄, R₅, R₆ and R₇ are different and at least one of them is selected from linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₉-C₁₅-alkenylarylalkoxy or N(R₈)₂ or SR₈ with R₈ being selected from linear or branched C₁-C₈-alkyl or linear or branched C₂-C₈-alkenyl or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom.
9. The process according to any one of claims 1 to 5 or 8, **characterized in that** one of R₃, R₄, R₅, R₆ and R₇ is linear or branched C₂-C₈-alkenyl, preferably C₂-C₆-alkenyl and most preferably C₂-C₃-alkenyl; C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy; or N(R₈)₂ or SR₈ with R₈ being selected from linear or branched C₁-C₈-alkyl or linear or branched C₂-C₈-alkenyl or R₈ form a C₃-C₉-alicyclic system together with the connecting N atom; and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl.
10. The process according to any one of claims 1 to 5 or 8, **characterized in that** two or three of R₃, R₄, R₅, R₆ and R₇ are linear or branched C₂-C₈-alkenyl, preferably C₂-C₆-alkenyl and most preferably C₂-C₃-alkenyl; C₁-C₈-alkoxy, preferably C₁-C₆-alkoxy and most preferably C₁-C₃-alkoxy; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy, and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl.
11. The process according to any one of claims 1 to 5, **characterized in that** R₃ and R₄ or R₄ and R₅ form an aromatic system together with the benzene ring of formula I, preferably a bicyclic, tricyclic or tetracyclic aromatic system, more preferably an aromatic system selected from a naphthyl, anthracenyl and phenanthrenyl system.
12. The process according to claim 11, **characterized in that** one of the remaining R is linear or branched C₂-C₈-alkenyl, preferably C₂-C₆-alkenyl and most preferably C₂-C₃-alkenyl; C₂-C₈-alkenyloxy, preferably C₂-C₆-alkenyloxy and most preferably C₃-C₅-alkenyloxy; and C₉-C₁₅-alkenylarylalkoxy, preferably C₉-C₁₂-alkenylarylalkoxy and most preferably C₉-C₁₀-alkenylarylalkoxy; and the remaining ones are independently selected from H and linear or branched C₁-C₈-alkyl, preferably linear or branched C₁-C₆-alkyl, more preferably linear or branched C₁-C₄-alkyl and most preferably linear C₁-C₃-alkyl.
13. The process according to any one of claims 1 to 12, **characterized in that** Z is OR₉ with R₉ being selected from H, linear or branched C₁-C₈-alkyl, linear or branched C₂-C₈-alkenyl, C₁-C₈-alkoxy, C₂-C₈-alkenyloxy, C₃-C₃-cycloalkyl, C₃-C₈-cycloalkoxy, C₇-C₁₅-arylalkoxy and C₉-C₁₅-alkenylarylalkoxy, preferably R₉ is H or Z is NR₁₀R₁₁ with R₁₀ and R₁₁ being independently selected from H, linear or branched C₁-C₈-alkyl, C₃-C₃-cycloalkyl, C₆-C₁₄-aryl, or R₁₀ and R₁₁ form a C₃-C₆-alicyclic system together with the connecting N atom, optionally one or more carbon atoms are replaced with O, preferably R₁₀ and R₁₁ form a C₅-C₆-alicyclic system together with the connecting N atom and one or more carbon atoms are replaced with O.
14. The process according to any one of claims 1 to 13, **characterized in that** the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is fully halogenated, preferably the at least partially halogenated C₂-C₈-alkane and/or C₂-C₈-alkene is selected from hexachloroethane, tetrachloroethylene and mixtures thereof.
15. The process according to any one of claims 1 to 14, **characterized in that** the base is selected from the group

comprising sodium hydroxide; lithium hydroxide;

potassium hydroxide; sodium C₁-C₆-alkoxide, preferably sodium C₁-C₄-alkoxide and most preferably sodium C₁-C₂-alkoxide; lithium C₁-C₆-alkoxide, preferably lithium C₁-C₄-alkoxide and most preferably lithium C₁-C₂-alkoxide; potassium C₁-C₆-alkoxide, preferably potassium C₁-C₄-alkoxide and most preferably potassium C₁-C₂-alkoxide; and mixtures thereof; or the base is selected from sodium C₁-C₆-alkoxide, preferably sodium C₁-C₄-alkoxide and most preferably sodium C₁-C₂-alkoxide; potassium C₁-C₆-alkoxide, preferably potassium C₁-C₄-alkoxide and most preferably potassium C₁-C₂-alkoxide, together with the protonated form of Z as defined above.

16. The process according to any one of claims 1 to 14, **characterized in that** the base is in form of an aqueous solution or the base is provided in an organic solvent, preferably the organic solvent is selected from the group comprising methanol, ethanol, n-propanol, tert.-butanol, dichloromethane, tetrachloroethylene, tetrahydrofuran, ethyl acetate, acetone, N,N-dimethylformamide, dimethylsulfoxide, dioxane, such as 1,3-dioxane or 1,4-dioxane, 1,2-dimethoxyethane, diethyleneglycol dimethyl ether, triethyleneglycol dimethyl ether and mixtures thereof.

17. The process according to any one of claims 1 to 16, **characterized in that** the process is carried out at a temperature of at least 30 °C, preferably in the range from 30 to 120 °C, more preferably in the range from 40 to 100 °C, and most preferably in the range from 40 to 90 °C.

18. The process according to any one of claims 1 to 17, **characterized in that** the process is carried out in an organic solvent, preferably the organic solvent is selected from the group comprising methanol, ethanol, n-propanol, tert.-butanol, dichloromethane, tetrachloroethylene, tetrahydrofuran, ethyl acetate, acetone, N,N-dimethylformamide, dimethylsulfoxide, dioxane, such as 1,3-dioxane or 1,4-dioxane, 1,2-dimethoxyethane, diethyleneglycol dimethyl ether, triethyleneglycol dimethyl ether and mixtures thereof.

19. The process according to any one of claims 1 to 18, **characterized in that** the process is carried out in the presence of a phase-transfer catalyst, preferably the phase-transfer catalyst is selected from a quaternary ammonium salt, tetraalkylphosphonium chloride, tetraalkylphosphonium bromide and mixtures thereof, preferably the phase-transfer catalyst is a tetraalkylammonium salt or a trialkylarylammonium salt, more preferably the phase-transfer catalyst is selected from the group comprising benzyltrimethylammonium hydroxide, benzyltriethylammonium chloride, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium hydrogensulfate, tetrabutylammonium hydroxide, methyltrioctylammonium chloride, cetyl pyridinium and mixtures thereof.

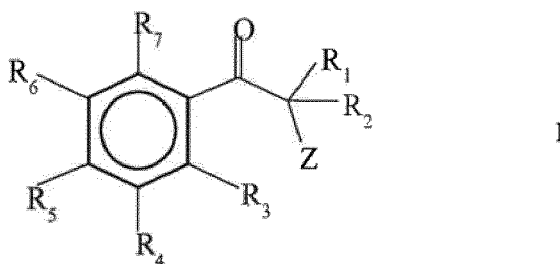
20. The process according to any one of claims 1 to 19, **characterized in that** the α -functionalized ketone is obtained in an one-pot reaction.

21. The process according to any one of claims 1 to 20, **characterized in that** the process further comprises a step of

- i) separating the obtained organic and aqueous phases, and/or
- ii) extracting the obtained aqueous phase with the organic solvent used in the process and combining the obtained organic phases, and/or
- (iii) acidifying the obtained organic phase to a pH of 3 to 6.5.

Patentansprüche

1. Verfahren zur Herstellung eines α -funktionalisierten Ketons der Formel



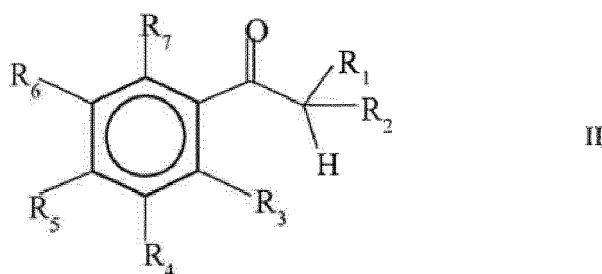
wobei R₁ und R₂ gleich oder verschieden sein können und unabhängig voneinander ausgewählt sind aus H, linearem

oder verzweigtem C₁-C₈-Alkyl, C₃-C₈-Cycloalkyl, linearem oder verzweigtem C₂-C₈-Alkenyl, C₅-C₈-Cycloalkenyl, linearem oder verzweigtem C₂-C₈-Alkinyl, C₆-C₁₄-Aryl oder zusammen mit dem verbrückenden C-Atom C₃-C₁₂-Cycloalkyl oder C₅-C₁₂-Cycloalkenyl bilden;

R₃, R₄, R₅, R₆ und R₇ gleich oder verschieden sein können und unabhängig voneinander ausgewählt sind aus H, linearem oder verzweigtem C₁-C₈-Alkyl, linearem oder verzweigtem C₂-C₈-Alkenyl, C₁-C₈-Alkoxy, C₂-C₈-Alkenyloxy, C₃-C₈-Cycloalkyl, C₆-C₁₄-Aryl, C₃-C₈-Cycloalkoxy, C₇-C₁₅-Arylalkoxy, C₉-C₁₅-Alkenylarylalkoxy, N(R₈)₂ oder SR₈, wobei R₈ ausgewählt ist aus linearem oder verzweigtem C₁-C₈-Alkyl, linearem oder verzweigtem C₂-C₈-Alkenyl, C₆-C₁₄-Aryl, C₁-C₈-Alkoxy, C₂-C₈-Alkenyloxy, C₃-C₈-Cycloalkyl, C₃-C₈-Cycloalkoxy, C₇-C₁₅-Arylalkoxy, C₉-C₁₅-Alkenylarylalkoxy, oder R₈ bildet ein C₃-C₉-alicyclisches System mit dem verbrückenden N-Atom, wobei optional ein oder mehrere Kohlenstoffatome durch O ersetzt werden, oder zwei benachbarte R mit dem Benzolring der Formel I ein aromatisches System bilden;

Z ist ausgewählt aus OR₉, NHR₉ und NR₁₀R₁₁ mit R₉, R₁₀ und R₁₁ unabhängig voneinander ausgewählt aus H, linearem oder verzweigtem C₁-C₈-Alkyl, linearem oder verzweigtem C₂-C₈-Alkenyl, C₁-C₈-Alkoxy, C₂-C₈-Alkenyloxy, C₃-C₈-Cycloalkyl, C₃-C₈-Cycloalkoxy, C₆-C₁₄-Aryl, C₇-C₁₅-Arylalkyl, C₇-C₁₅-Arylalkoxy, C₉-C₁₅-Alkenylarylalkoxy, C₉-C₁₅-Alkenylarylalkyl; oder R₁₀ und R₁₁ bilden ein C₃-C₉-alicyclisches System mit dem verbrückenden N oder C-Atom, wobei optional ein oder mehrere Kohlenstoffatome durch O ersetzt werden;

dadurch gekennzeichnet, dass ein Keton der allgemeinen Formel II



wobei R₁, R₂, R₃, R₄, R₅, R₆ und R₇ wie oben definiert sind, unter Phasen-Transfer-Bedingungen mit einem zumindest teilweise halogenierten C₂-C₈-Alkan und/oder C₂-C₈-Alken in Kontakt gebracht wird, und

i) eine Base ausgewählt aus der Gruppe bestehend aus Alkalimetall Hydroxid, Erdalkalimetall Hydroxid, Alkalimetall C₁-C₈-Alkoxide, Erdalkalimetall C₁-C₈-Alkoxid und Gemischen aus diesen, oder

ii) eine Base ausgewählt aus der Gruppe enthaltend Alkalimetall Hydroxid, Erdalkalimetall Hydroxid, Alkalimetall C₁-C₈-Alkoxid, Erdalkalimetall C₁-C₈-Alkoxid und Gemischen aus diesen zusammen mit der protonierten Form von Z wie oben definiert.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** R₁ und R₂ gleich sind.

3. Verfahren nach Anspruch 2, **dadurch gekennzeichnet, dass** R₁ und R₂ ausgewählt sind aus H und linearem oder verzweigtem C₁-C₈-Alkyl, bevorzugt linearem oder verzweigtem C₁-C₆-Alkyl, mehr bevorzugt linearem oder verzweigtem C₁-C₄-Alkyl und am meisten bevorzugt linearem C₁-C₃-Alkyl.

4. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** R₁ und R₂ verschieden sind und unabhängig voneinander ausgewählt sind aus linearem oder verzweigtem C₁-C₈-Alkyl, bevorzugt linearem oder verzweigtem C₁-C₆-Alkyl, mehr bevorzugt lineares oder verzweigtes C₁-C₄-Alkyl und am meisten bevorzugt linearem C₁-C₃-Alkyl.

5. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** R₁ und R₂ C₄-C₁₀-Cycloalkyl, bevorzugt C₄-C₈-Cycloalkyl, und am meisten bevorzugt C₆-Cycloalkyl mit dem verbrückenden C-Atom bilden.

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** R₃, R₄, R₅, R₆ und R₇ gleich sind.

7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, dass** R₃, R₄, R₅, R₆ und R₇ ausgewählt sind aus H und linearem oder verzweigtem C₁-C₈-Alkyl, bevorzugt linearem oder verzweigtem C₁-C₆-Alkyl, mehr bevorzugt linearem oder verzweigtem C₁-C₄-Alkyl und am meisten bevorzugt linearem C₁-C₃-Alkyl.

8. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** R₃, R₄, R₅, R₆ und R₇ verschieden

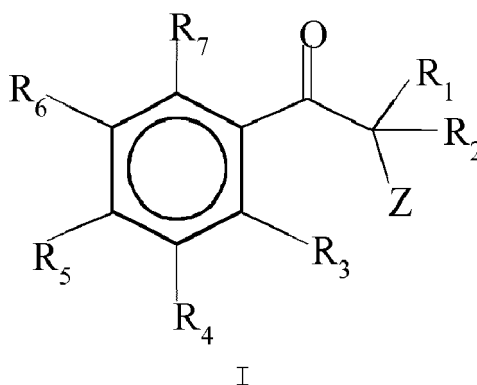
sind und mindestens einer von ihnen ausgewählt ist aus linearem oder verzweigtem C₁-C₈-Alkyl, linearem oder verzweigtem C₂-C₃-Alkenyl, C₁-C₈-Alkoxy, C₂-C₈-Alkenyloxy, C₉-C₁₅-Alkenylarylalkoxy oder N(R₈)₂ oder SR₈ mit R₈ ausgewählt aus linearem oder verzweigtem C₁-C₈-Alkyl oder linearem oder verzweigtem C₂-C₈-Alkenyl oder R₈ bildet ein C₃-C₉-alicyclisches System mit dem verbrückenden N-Atom.

- 5
9. Verfahren nach einem der Ansprüche 1 bis 5 oder 8, **dadurch gekennzeichnet, dass** einer von R₃, R₄, R₅, R₆ und R₇ linear oder verzweigtes C₂-C₈-Alkenyl, bevorzugt C₂-C₆-Alkenyl und am meisten bevorzugt C₂-C₃-Alkenyl ist; C₁-C₈-Alkoxy, bevorzugt C₁-C₆-Alkoxy, am meisten bevorzugt C₁-C₃-Alkoxy; C₂-C₈-Alkenyloxy, bevorzugt C₂-C₆-Alkenyloxy, am meisten bevorzugt C₃-C₅-Alkenyloxy; C₉-C₁₅-Alkenylarylalkoxy, bevorzugt C₉-C₁₂-Alkenylarylalkoxy, am meisten bevorzugt C₉-C₁₀-Alkenylarylalkoxy ist; oder N(R₈)₂ oder SR₈ mit R₈ ausgewählt aus linearem oder verzweigtem C₁-C₈-Alkyl oder linearem oder verzweigtem C₂-C₈-Alkenyl oder R₈ ein C₃-C₉-alicyclisches System mit dem verbrückenden N-Atom bildet; und die übrigen unabhängig voneinander ausgewählt sind aus H und linearem oder verzweigtem C₁-C₈-Alkyl, bevorzugt linearem oder verzweigtem C₁-C₆-Alkyl, mehr bevorzugt linearem oder verzweigtem C₁-C₄-Alkyl und am meisten bevorzugt linearem C₁-C₃-Alkyl.
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10. Verfahren nach einem der Ansprüche 1 bis 5 oder 8, **dadurch gekennzeichnet, dass** zwei oder drei von R₃, R₄, R₅, R₆ und R₇ linear oder verzweigtes C₂-C₈-Alkenyl, bevorzugt C₂-C₆-Alkenyl und am meisten bevorzugt C₂-C₃-Alkenyl sind; C₁-C₈-Alkoxy, bevorzugt C₁-C₆-Alkoxy, und am meisten bevorzugt C₁-C₃-Alkoxy sind; C₂-C₈-Alkenyloxy, bevorzugt C₂-C₅-Alkenyloxy, und am meisten bevorzugt C₃-C₅-Alkenyloxy sind; und C₉-C₁₅-Alkenylarylalkoxy, bevorzugt C₉-C₁₂-Alkenylarylalkoxy und am meisten bevorzugt C₉-C₁₀-Alkenylarylalkoxy sind, und die übrigen unabhängig voneinander ausgewählt sind aus H und linearem oder verzweigtem C₁-C₈-Alkyl, bevorzugt linearem oder verzweigtem C₁-C₆-Alkyl, mehr bevorzugt linearem oder verzweigtem C₁-C₄-Alkyl, und am meisten bevorzugt linearem C₁-C₃-Alkyl.
- 20
11. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** R₃ und R₄ oder R₄ und R₅ ein aromatisches System bilden mit dem Benzolring der Formel I, bevorzugt ein bicyclisches, tricyclisches oder tetracyclisches aromatisches System, mehr bevorzugt ein aromatisches System ausgewählt aus einem Naphthyl, Anthracenyl und Phenanthrenyl.
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12. Verfahren nach Anspruch 11, **dadurch gekennzeichnet, dass** einer der übrigen R lineares oder verzweigtes C₂-C₈-Alkenyl, bevorzugt C₂-C₆-Alkenyl, und am meisten bevorzugt C₂-C₃-Alkenyl ist; C₂-C₈-Alkenyloxy, bevorzugt C₂-C₆-Alkenyloxy und besonders bevorzugt C₃-C₅-Alkenyloxy ist; und C₉-C₁₅-Alkenylarylalkoxy, bevorzugt C₉-C₁₂-Alkenylarylalkoxy und besonders bevorzugt C₉-C₁₀-Alkenylarylalkoxy ist; und die übrigen unabhängig voneinander ausgewählt sind aus H und linearem oder verzweigtem C₁-C₈-Alkyl, bevorzugt linearem oder verzweigtem C₁-C₆-Alkyl, mehr bevorzugt linearem oder verzweigtem C₁-C₄-Alkyl und besonders bevorzugt linearem C₁-C₃-Alkyl.
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13. Verfahren nach einem der Ansprüche 1 bis 12, **dadurch gekennzeichnet, dass** Z OR₉ ist wobei R₉ ausgewählt ist aus H, linearem oder verzweigtem C₁-C₈-Alkyl, linearem oder verzweigtem C₂-C₈-Alkenyl, C₁-C₈-Alkoxy, C₂-C₈-Alkenyloxy, C₃-C₈-Cycloalkyl, C₃-C₈-Cycloalkoxy, C₇-C₁₅-Arylalkoxy und C₉-C₁₅-Alkenylarylalkoxy, wobei R₉ bevorzugt H ist oder Z ist NR₁₀R₁₁ mit R₁₀ und R₁₁ unabhängig voneinander ausgewählt aus H, linearem oder verzweigtem C₁-C₈-Alkyl, C₃-C₈-Cycloalkyl, C₆-C₁₄-Aryl, oder R₁₀ und R₁₁ bilden ein C₃-C₆-alicyclisches System mit dem verbrückenden N-Atom, wobei optional ein oder mehrere Kohlenstoffatome durch O ersetzt werden, R₁₀ und R₁₁ vorzugsweise mit dem verbrückenden N-Atom ein C₅-C₆-alicyclisches System bilden und ein oder mehrere Kohlenstoffatome durch O ersetzt sind.
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14. Verfahren nach einem der Ansprüche 1 bis 13, **dadurch gekennzeichnet, dass** das zumindest teilweise halogenierte C₂-C₈-Alkan und/oder C₂-C₈-Alken vollständig halogeniert ist, bevorzugt ist das zumindest teilweise halogenierte C₂-C₈-Alkan und/oder C₂-C₈-Alken ausgewählt aus Hexachlorethan, Tetrachlorethylen und Gemischen aus diesen.
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15. Verfahren nach einem der Ansprüche 1 bis 14, **dadurch gekennzeichnet, dass** die Base ausgewählt ist aus der Gruppe umfassend Natriumhydroxid; Lithiumhydroxid; Kaliumhydroxid; Natrium C₁-C₆-Alkoxid, bevorzugt Natrium C₁-C₄-Alkoxid und am meisten bevorzugt Natrium C₁-C₂-Alkoxid; Lithium C₁-C₆-Alkoxid, bevorzugt Lithium C₁-C₄-Alkoxid und am meisten bevorzugt Lithium C₁-C₂-Alkoxid, Kalium C₁-C₆-Alkoxid, bevorzugt Kalium C₁-C₄-Alkoxid und am meisten bevorzugt Kalium C₁-C₂-Alkoxid; und Gemische aus diesen; oder die Base ist ausgewählt aus Natrium C₁-C₆-Alkoxid, bevorzugt Natrium C₁-C₄-Alkoxid und am meisten bevorzugt Natrium C₁-C₂-Alkoxid; Kalium C₁-C₆-Alkoxid, bevorzugt Kalium C₁-C₄-Alkoxid und am meisten bevorzugt Kalium C₁-C₂-Alkoxid zusammen mit der protonierten Form von Z wie oben definiert.
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16. Verfahren nach einem der Ansprüche 1 bis 14, **dadurch gekennzeichnet, dass** die Base in Form einer wässrigen Lösung oder in einem organischen Lösungsmittel bereitgestellt wird, wobei das organische Lösungsmittel bevorzugt ausgewählt ist aus der Gruppe umfassend Methanol, Ethanol, n-Propanol, tert.-Butanol, Dichlormethan, Tetrachlorethylen, Tetrahydrofuran, Ethylacetat, Aceton, N,N-Dimethylformamid, Dimethylsulfoxid, Dioxan, wie 1,3-Dioxan oder 1,4-Dioxan, 1,2-Dimethoxyethan, Diethylenglycoldimethylether, Triethylenglycoldimethylether und Gemischen aus diesen.
17. Verfahren nach einem der Ansprüche 1 bis 16, **dadurch gekennzeichnet, dass** das Verfahren bei einer Temperatur von mindestens 30 °C, bevorzugt im Bereich von 30 bis 120 °C, mehr bevorzugt im Bereich von 40 bis 100 °C, am meisten bevorzugt im Bereich von 40 bis 90 °C durchgeführt wird.
18. Verfahren nach einem der Ansprüche 1 bis 18, **dadurch gekennzeichnet, dass** das Verfahren in einem organischen Lösungsmittel durchgeführt wird, wobei das organische Lösungsmittel bevorzugt ausgewählt ist aus der Gruppe umfassend Methanol, Ethanol, n-Propanol, tert.-Butanol, Dichlormethan, Tetrachlorethylen, Tetrahydrofuran, Ethylacetat, Aceton, N,N-Dimethylformamid, Dimethylsulfoxid, Dioxan, wie 1,3-Dioxan oder 1,4-Dioxan, 1,2-Dimethoxyethan, Diethylenglycoldimethylether, Triethylenglycoldimethylether und Gemischen aus diesen.
19. Verfahren nach einem der Ansprüche 1 bis 18, **dadurch gekennzeichnet, dass** das Verfahren in Gegenwart eines Phasen-Transfer Katalysators durchgeführt wird, wobei der Phasen-Transfer Katalysator bevorzugt ausgewählt ist aus einem quartären Ammoniumsalz, Tetraalkylphosphoniumchlorid, Tetraalkylphosphoniumbromid und Gemischen aus diesen, wobei der Phasen-Transfer Katalysator bevorzugt ein Tetraalkylammoniumsalz oder ein Trialkylarylammoniumsalz ist, mehr bevorzugt ist der Phasen-Transfer Katalysator ausgewählt aus der Gruppe umfassend Benzyltrimethylammonium Hydroxid, Benzyltriethylammonium Chlorid, Tetrabutylammonium Chlorid, Tetrabutylammonium Bromid, Tetrabutylammonium Hydrogensulfat, Tetrabutylammonium Hydroxid, Methyltriocetylammmonium Chlorid, Cetyl Pyridinium und Gemischen aus diesen.
20. Verfahren nach einem der Ansprüche 1 bis 19, **dadurch gekennzeichnet, dass** das α -funktionalisierte Keton in einer Eintopfreaktion erhalten wird.
21. Verfahren nach einem der Ansprüche 1 bis 20, **dadurch gekennzeichnet, dass** das Verfahren den zusätzlichen Schritt
- i) Trennung der erhaltenen organischen und wässrigen Phasen, und/oder
 - ii) Extrahieren der erhaltenen wässrigen Phase mit dem organischen Lösungsmittel welches im Verfahren verwendet wurde und vereinigen der erhaltenen organischen Phasen, und/oder
 - iii) Ansäuern der erhaltenen organischen Phase auf einen pH-Wert von 3 bis 6,5.

Revendications

1. Procédé pour la préparation d'une cétone α -fonctionnalisée de formule générale I,



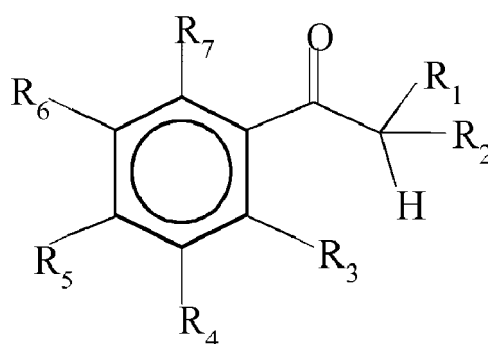
dans laquelle R_1 et R_2 sont identiques ou différents et sont indépendamment choisis parmi H, alkyle en C_1 à C_8

linéaire ou ramifié, cycloalkyle en C₃ à C₈, alcényle en C₂ à C₈ linéaire ou ramifié, cycloalcényle en C₅ à C₈, alcynyle en C₂ à C₈ linéaire ou ramifié, aryle en C₆ à C₁₄, ou forment un cycloalkyle en C₃ à C₁₂ ou cycloalcényle en C₅ à C₁₂ conjointement avec l'atome C de connexion ;

R₃, R₄, R₅, R₆ et R₇ sont identiques ou différents et sont indépendamment choisis parmi H, alkyle en C₁ à C₈ linéaire ou ramifié, alcényle en C₂ à C₈ linéaire ou ramifié, alcoxy en C₁ à C₈, alcényloxy en C₂ à C₈, cycloalkyle en C₃ à C₈, aryle en C₆ à C₁₄, cycloalcoxy en C₃ à C₈, arylalcoxy en C₇ à C₁₅, alcénylarylalcoxy en C₉ à C₁₅, N(R₈)₂ ou SR₈ où R₈ est choisi parmi alkyle en C₁ à C₈ linéaire ou ramifié, alcényle en C₂ à C₈ linéaire ou ramifié, aryle en C₆ à C₁₄, alcoxy en C₁ à C₈, alcényloxy en C₂ à C₈, cycloalkyle en C₃ à C₈, cycloalcoxy en C₃ à C₈, arylalcoxy en C₇ à C₁₅, alcénylarylalcoxy en C₉ à C₁₅, ou bien les R₈ forment un système alicyclique en C₃ à C₉ conjointement avec l'atome N de connexion, optionnellement un ou plusieurs atomes de carbone sont remplacés par O, ou bien deux R adjacents forment un système aromatique conjointement avec le cycle benzène de la formule I ;

Z est choisi parmi OR₉, NHR₉ et NR₁₀R₁₁ où R₉, R₁₀ et R₁₁ sont indépendamment choisis parmi H, alkyle en C₁ à C₈ linéaire ou ramifié, alcényle en C₂ à C₈ linéaire ou ramifié, alcoxy en C₁ à C₈, alcényloxy en C₂ à C₈, cycloalkyle en C₃ à C₈, cycloalcoxy en C₃ à C₈, aryle en C₆ à C₁₄, arylalkyle en C₇ à C₁₅, arylalcoxy en C₇ à C₁₅, alcénylarylalcoxy en C₉ à C₁₅, alcénylarylalkyle en C₉ à C₁₅ ; ou bien R₁₀ et R₁₁ forment un système alicyclique en C₃ à C₉ conjointement avec l'atome N ou C de connexion, optionnellement un ou plusieurs atomes de carbone sont remplacés par O ;

caractérisé en ce qu'une cétone de formule générale II



II

dans laquelle R₁, R₂, R₃, R₄, R₅, R₆ et R₇ sont tels que définis ci-dessus, est mise en contact dans des conditions de transfert de phase avec un alcane en C₂ à C₈ et/ou alcène en C₂ à C₈ au moins partiellement halogéné, et

i) une base choisie dans le groupe comprenant un hydroxyde de métal alcalin, un hydroxyde de métal alcalino-terreux, un alkylate en C₁ à C₈ de métal alcalin, un alkylate en C₁ à C₈ de métal alcalino-terreux, et leurs mélanges, ou

ii) une base choisie dans le groupe comprenant un hydroxyde de métal alcalin, un hydroxyde de métal alcalino-terreux, un alkylate en C₁ à C₈ de métal alcalin, un alkylate en C₁ à C₈ de métal alcalino-terreux, et leurs mélanges, conjointement avec la forme protonée de Z tel que défini ci-dessus.

2. Procédé selon la revendication 1, **caractérisé en ce que** R₁ et R₂ sont identiques.

3. Procédé selon la revendication 2, **caractérisé en ce que** R₁ et R₂ sont choisis parmi H et alkyle en C₁ à C₈ linéaire ou ramifié, de préférence alkyle en C₁ à C₈ linéaire ou ramifié, plus préférablement alkyle en C₁ à C₄ linéaire ou ramifié et le plus préférablement alkyle en C₁ à C₃ linéaire.

4. Procédé selon la revendication 1, **caractérisé en ce que** R₁ et R₂ sont différents et sont indépendamment choisis parmi H et alkyle en C₁ à C₈ linéaire ou ramifié, de préférence alkyle en C₁ à C₈ linéaire ou ramifié, plus préférablement alkyle en C₁ à C₄ linéaire ou ramifié et le plus préférablement alkyle en C₁ à C₃ linéaire.

5. Procédé selon la revendication 1, **caractérisé en ce que** R₁ et R₂ forment un cycloalkyle en C₄ à C₁₀ de préférence cycloalkyle en C₄ à C₈, et le plus préférablement cycloalkyle en C₆, conjointement avec l'atome C de connexion.

6. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** R₃, R₄, R₅, R₆ et R₇ sont identiques.

7. Procédé selon la revendication 6, **caractérisé en ce que** R₃, R₄, R₅, R₆ et R₇ sont choisis parmi H et alkyle en C₁

à C₈ linéaire ou ramifié, de préférence alkyle en C₁ à C₆ linéaire ou ramifié, plus préférablement alkyle en C₁ à C₄ linéaire ou ramifié et le plus préférablement alkyle en C₁ à C₃ linéaire.

8. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** R₃, R₄, R₅, R₆ et R₇ sont différents et au moins l'un d'eux est choisi parmi alkyle en C₁ à C₈ linéaire ou ramifié, alcényle en C₂ à C₈ linéaire ou ramifié, alcoxy en C₁ à C₈, alcényloxy en C₂ à C₈, alcénylarylalcoxy en C₉ à C₁₅, N(R₈)₂ et SR₈, où R₈ est choisi parmi alkyle en C₁ à C₈ linéaire ou ramifié et alcényle en C₂ à C₈ linéaire ou ramifié, ou bien les R₈ forment un système alicyclique en C₃ à C₉ conjointement avec l'atome N de connexion.

9. Procédé selon l'une quelconque des revendications 1 à 5 et 8, **caractérisé en ce que** l'un parmi R₃, R₄, R₅, R₆ et R₇ est un alcényle en C₂ à C₈ linéaire ou ramifié, de préférence alcényle en C₂ à C₆ et le plus préférablement alcényle en C₂ à C₃; alcoxy en C₁ à C₈, de préférence alcoxy en C₁ à C₆ et le plus préférablement alcoxy en C₁ à C₃; alcényloxy en C₂ à C₈, de préférence alcényloxy en C₂ à C₆ et le plus préférablement alcényloxy en C₃ à C₅; alcénylarylalcoxy en C₉ à C₁₅, de préférence alcénylarylalcoxy en C₉ à C₁₂ et le plus préférablement alcénylarylalcoxy en C₉ à C₁₀; ou N(R₈)₂ ou SR₈ où R₈ est choisi parmi alkyle en C₁ à C₈ linéaire ou ramifié et alcényle en C₂ à C₈ linéaire ou ramifié, ou bien les R₈ forment un système alicyclique en C₃ à C₉ conjointement avec l'atome N de connexion; et ceux restants sont indépendamment choisis parmi H et alkyle en C₁ à C₈ linéaire ou ramifié, de préférence alkyle en C₁ à C₆ linéaire ou ramifié, plus préférablement alkyle en C₁ à C₄ linéaire ou ramifié et le plus préférablement alkyle en C₁ à C₃ linéaire.

10. Procédé selon l'une quelconque des revendications 1 à 5 et 8, **caractérisé en ce que** deux ou trois parmi R₃, R₄, R₅, R₆ et R₇ sont un alcényle en C₂ à C₈ linéaire ou ramifié, de préférence alcényle en C₂ à C₆ et le plus préférablement alcényle en C₂ à C₃; alcoxy en C₁ à C₈, de préférence alcoxy en C₁ à C₆ et le plus préférablement alcoxy en C₁ à C₃; alcényloxy en C₂ à C₈, de préférence alcényle en C₂ à C₆ et le plus préférablement alcényloxy en C₃ à C₅; alcénylarylalcoxy en C₉ à C₁₅, de préférence alcénylarylalcoxy en C₉ à C₁₂ et le plus préférablement alcénylarylalcoxy en C₉ à C₁₀, et ceux restants sont indépendamment choisis parmi H et alkyle en C₁ à C₈ linéaire ou ramifié, de préférence alkyle en C₁ à C₆ linéaire ou ramifié, plus préférablement alkyle en C₁ à C₄ linéaire ou ramifié et le plus préférablement alkyle en C₁ à C₃ linéaire.

11. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** R₃ et R₄ ou R₄ et R₅ forment un système aromatique conjointement avec le cycle benzène de la formule I, de préférence un système aromatique bicyclique, tricyclique ou tétracyclique, plus préférablement un système aromatique choisi parmi les systèmes naphthyle, anthracényle et phénanthrényle.

12. Procédé selon la revendication 11, **caractérisé en ce que** l'un des R restants est un alcényle en C₂ à C₈ linéaire ou ramifié, de préférence alcényle en C₂ à C₆ et le plus préférablement alcényle en C₂ à C₃; alcényloxy en C₂ à C₈, de préférence alcényloxy en C₂ à C₆ et le plus préférablement alcényloxy en C₃ à C₅; ou alcénylarylalcoxy en C₉ à C₁₅, de préférence alcénylarylalcoxy en C₉ à C₁₂ et le plus préférablement alcénylarylalcoxy en C₉ à C₁₀; et ceux restants sont indépendamment choisis parmi H et alkyle en C₁ à C₈ linéaire ou ramifié, de préférence alkyle en C₁ à C₆ linéaire ou ramifié, plus préférablement alkyle en C₁ à C₄ linéaire ou ramifié et le plus préférablement alkyle en C₁ à C₃ linéaire.

13. Procédé selon l'une quelconque des revendications 1 à 12, **caractérisé en ce que** Z est OR₉ où R₉ est choisi parmi H, alkyle en C₁ à C₈ linéaire ou ramifié, alcényle en C₂ à C₈ linéaire ou ramifié, alcoxy en C₁ à C₈, alcényloxy en C₂ à C₈, cycloalkyle en C₃ à C₈, cycloalcoxy en C₃ à C₈, arylalcoxy en C₇ à C₁₅ et alcénylarylalcoxy en C₉ à C₁₅, de préférence R₉ est H ou Z est NR₁₀R₁₁ où R₁₀ et R₁₁ sont indépendamment choisis parmi H, alkyle en C₁ à C₈ linéaire ou ramifié, cycloalkyle en C₃ à C₈, aryle en C₆ à C₁₄, ou bien R₁₀ et R₁₁ forment un système alicyclique en C₃ à C₆ conjointement avec l'atome N de connexion, optionnellement un ou plusieurs atomes de carbone sont remplacés par O, de préférence R₁₀ et R₁₁ forment un système alicyclique en C₅ à C₆ conjointement avec l'atome N de connexion et un ou plusieurs atomes de carbone sont remplacés par O.

14. Procédé selon l'une quelconque des revendications 1 à 13, **caractérisé en ce que** l'alcane en C₂ à C₈ et/ou alcène en C₂ à C₈ au moins partiellement halogéné est complètement halogéné, de préférence l'alcane en C₂ à C₈ et/ou alcène en C₂ à C₈ est choisi parmi l'hexachloroéthane, le tétrachloroéthylène et leurs mélanges.

15. Procédé selon l'une quelconque des revendications 1 à 14, **caractérisé en ce que** la base est choisie dans le groupe comprenant l'hydroxyde de sodium; l'hydroxyde de lithium; l'hydroxyde de potassium; un alkylate de sodium en C₁ à C₆, de préférence un alkylate de sodium en C₁ à C₄ et le plus préférablement un alkylate de sodium

en C₁ à C₂ ; un alkylate de lithium en C₁ à C₆, de préférence un alkylate de lithium en C₁ à C₄ et le plus préférablement un alkylate de lithium en C₁ à C₂ ; un alkylate de potassium en C₁ à C₆, de préférence un alkylate de potassium en C₁ à C₄ et le plus préférablement un alkylate de potassium en C₁ à C₂ ; et leurs mélanges ; ou bien la base est choisie parmi un alkylate de sodium en C₁ à C₆, de préférence un alkylate de sodium en C₁ à C₄ et le plus préférablement un alkylate de sodium en C₁ à C₂ ; un alkylate de potassium en C₁ à C₆, de préférence un alkylate de potassium en C₁ à C₄ et le plus préférablement un alkylate de potassium en C₁ à C₂, conjointement avec la forme protonée de Z tel que défini ci-dessus.

16. Procédé selon l'une quelconque des revendications 1 à 14, **caractérisé en ce que** la base est sous la forme d'une solution aqueuse ou bien la base est disposée dans un solvant organique, de préférence le solvant organique est choisi dans le groupe comprenant le méthanol, l'éthanol, le n-propanol, le tert-butanol, le dichlorométhane, le tétrachloroéthylène, le tétrahydrofurane, l'acétate d'éthyle, l'acétone, le N,N-diméthylformamide, le diméthylsulfoxyde, le dioxane, tel que le 1,3-dioxane ou le 1,4-dioxane, le 1,2-diméthoxyéthane, l'éther diméthylique de diéthylèneglycol, l'éther diméthylique de triéthylèneglycol et leurs mélanges.

17. Procédé selon l'une quelconque des revendications 1 à 16, **caractérisé en ce que** le procédé est mis en œuvre à une température d'au moins 30°C, de préférence dans la plage de 30 à 120°C, plus préférablement dans la plage de 40 à 100°C, et le plus préférablement dans la plage de 40 à 90°C.

18. Procédé selon l'une quelconque des revendications 1 à 17, **caractérisé en ce que** le procédé est mis en œuvre dans un solvant organique, de préférence le solvant organique est choisi dans le groupe comprenant le méthanol, l'éthanol, le n-propanol, le tert-butanol, le dichlorométhane, le tétrachloroéthylène, le tétrahydrofurane, l'acétate d'éthyle, l'acétone, le N,N-diméthylformamide, le diméthylsulfoxyde, le dioxane, tel que le 1,3-dioxane ou le 1,4-dioxane, le 1,2-diméthoxyéthane, l'éther diméthylique de diéthylèneglycol, l'éther diméthylique de triéthylèneglycol et leurs mélanges.

19. Procédé selon l'une quelconque des revendications 1 à 18, **caractérisé en ce que** le procédé est mis en œuvre en présence d'un catalyseur de transfert de phase, de préférence le catalyseur de transfert de phase est choisi parmi un sel d'ammonium quaternaire, un chlorure de tétraalkylphosphonium, un bromure de tétraalkylphosphonium et leurs mélanges, de préférence le catalyseur de transfert de phase est un sel de tétraalkylammonium ou un sel de trialkylarylammonium, plus préférablement le catalyseur de transfert de phase est choisi dans le groupe comprenant l'hydroxyde de benzyltriméthylammonium, le chlorure de benzyltriéthylammonium, le chlorure de tétrabutylammonium, le bromure de tétrabutylammonium, l'hydrogénosulfate de tétrabutylammonium, l'hydroxyde de tétrabutylammonium, le chlorure de méthyltriocetylammmonium, le cetylpyridinium et leurs mélanges.

20. Procédé selon l'une quelconque des revendications 1 à 19, **caractérisé en ce que** la cétone α -fonctionnalisée est obtenue dans une réaction monotope.

21. Procédé selon l'une quelconque des revendications 1 à 20, **caractérisé en ce que** le procédé comprend en outre une étape de

- i) séparation des phases organique et aqueuse obtenues, et/ou
- ii) extraction de la phase aqueuse obtenue avec le solvant organique utilisé dans le procédé et combinaison des phases organiques obtenues, et/ou
- iii) acidification de la phase organique obtenue à un pH de 3 à 6,5.

REFERENCES CITED IN THE DESCRIPTION

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