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(54) Title: PROCESS FOR THE PREPARATION OF BETA-GAMMA ENE CARBONYL DERIVATIVES

(57) Abstract: The present invention relates to a preparation of β-γ ene carboxylic or ketone derivatives, which may also have particular requirement on the configuration of the carbon-carbon double bond. The method requires a thermal treatment of α-β unsaturated malonate or acetylacetonate derivatives in the presents of at least one carboxylic acid and at least one alkaline, alkaline-earth or lanthanide halide or carboxylates.

PROCESS FOR THE PREPARATION OF β–γ ENE CARBONYL DERIVATIVES

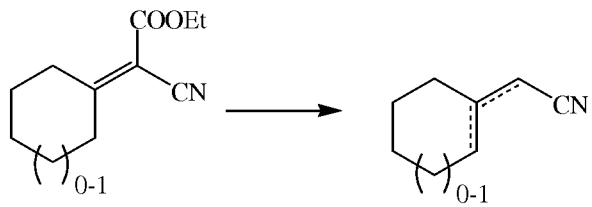
Technical field

The present invention relates to the field of organic chemistry and, more particularly, to the preparation of β–γ ene carbonyl derivatives, which may also have particular requirement on the configuration of the carbon-carbon double bond.

Prior Art

The preparation of tri- or tetra substituted β-γ unsaturated ester or ketone derivatives by elimination on an acyl or carboxylic esters of an α-β unsaturated geminal dicarbonyl derivative is reported only in one reference (see V.Venkateswaran *et al.* in Tetrahedron Letters, **1979**, 553.

In this article the authors report a reaction according to the following scheme:



however, with this methodology the authors in two cases obtain a product wherein the major isomer is the α–β unsaturated derivative, to the contrary of the present invention, and in one case obtain a product wherein the major isomer is the β-γ unsaturated derivative, however with a poor selectivity.

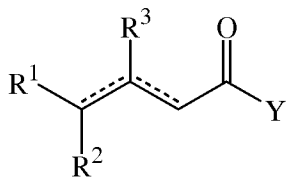
In Helv.Chem-Acta, **1992**, 759, by K. Schulte-Elte *et al.*, there is disclosed a synthesis of 5,6-dimethylhept-4-en-2-one (with a β-γ/α-β ratio of about 13 and a β-γ E/Z ratio of about 2.2) by the demethoxycarbonylation of the corresponding alkylidene acetoacetate in the presence of DMSO, water and LiCl. Although the selectivities provided by this method are higher than the ones reported above, there is still an interested or need in improving them.

Indeed β-γ unsaturated ketones or esters can be useful intermediates in the preparation of important chemicals, there is still a need for a new or alternative process

which allows their preparation with a good selectivity and therefore an increased yield. Furthermore, it is also important to prepare the desired β-γ unsaturated ketones or esters with a good selectivity in the configuration of the double bond, as it is sometime desired to obtain a product with a high content of the (E)- β-γ isomer.

Description of the invention

In order to overcome the problems aforementioned, the present invention relates to processes for the preparation of a compound of formula (I)



(I)

wherein the dotted lines indicate that the compound is in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives, the molar ratio β–γ/α–β being at least 3;

Y represent, independently of each other, a OR^4 or R^4 group, R^4 representing a C_1-C_8 hydrocarbon group, optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

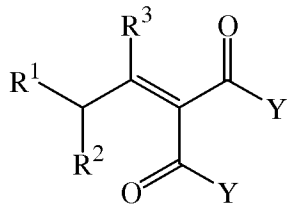
R^1 represents a C_1-C_{15} hydrocarbon group, optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

R^2 represents a C_1-C_5 hydrocarbon group, optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

R^3 represents a hydrogen atom or a C_1-C_5 hydrocarbon group; and

optionally said R_1 and R_2, and/or R_1 and R_3, taken together may form a C_4-C_{12} hydrocarbon group optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

said method comprising the step of reacting, at a temperature comprised between 100°C and 230°C, a compound of formula



(II)

wherein Y, R^1, R^2 and R^3 are defined as in formula (I);

with at least one compound from the group i) and at least one compound from the group ii), said groups consisting respectively of:

i) the salts of formula MX_2, $M''X_3$ or $M'X$, wherein M is an alkali-earth cation and M' an alkali cation or C_0-C_{12} ammonium cation and M" is a lanthanide cation, and X is a halide or an anion of an acid HX having a pK_a comprised between 0 and 6;

ii) the carboxylic acids of formula R^5COOH, wherein R^5 represents a C_1-C_{18} hydrocarbon group optionally comprising one or two oxygen atoms;

and optionally in the presence of a polar aprotic solvent having a boiling point of above 100°C.

According to an embodiment of the invention, the process concerns the preparation of a compound (I), starting from the corresponding compound (II), wherein :

the dotted lines indicate that the compound is in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives, the molar ratio β–γ/α–β being at least 3;

Y represent, independently of each other, a OR^4 or R^4 group, R^4 representing a C_1-C_6 alkyl group a phenyl group or a benzyl group;

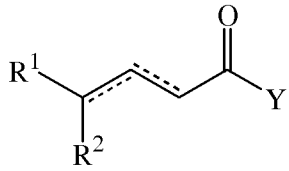
R^1 represents a C_2-C_{12} hydrocarbon atom, optionally comprising 1 to 3 functional hetero atoms selected from the group consisting of oxygen, sulfur and nitrogen;

R^2 represents a C_1-C_3 alkyl atom;

R^3 represents a hydrogen atom or a C_1-C_3 alkyl group; and

optionally said R_1 and R_2, and/or R_1 and R_3, taken together may form a C_5-C_{12} hydrocarbon atom optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen.

According to another embodiment of the invention, the compound of formula (I) is of formula



(III)

the dotted lines indicate that the compound is in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives, the molar ratio β–γ/α–β being at least 3;

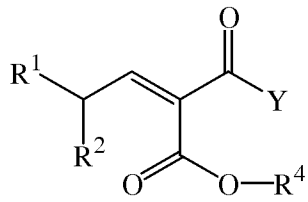
Y represent, independently of each other, a OR^4 or R^4 group, R^4 representing a C_1-C_6 alkyl group or a C_6-C_{10} phenyl or benzyl group optionally comprising 1 to 3 oxygen or nitrogen atoms;

R^1 represents a C_2-C_{12} hydrocarbon atom, optionally comprising 1 to 3 functional oxygen or nitrogen atoms;

R^2 represents a C_1-C_3 alkyl group;

optionally said R_1 and R_2, taken together may form a C_4-C_{11} hydrocarbon group optionally comprising 1 to 3 oxygen or nitrogen atoms.

Said compound of formula (III) are obtainable by the method according the invention by reacting, under the described condition, a compound of formula



(IV)

wherein Y, R^1, R^2 and R^4 are defined as in formula (III).

According to any of the above-mentioned embodiments of the invention, the invention's process can be particularly useful when using compounds (II) wherein at least one Y is a OR^4 group, or even the two Y are OR^4 groups.

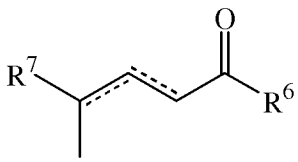
According to any of the above-mentioned embodiments of the invention, said hydrocarbon group is in the form of an alkyl, alkenyl, alkandienyl, aryl group or a mixture thereof, and said hydrocarbon group can be a linear, branched, cyclic group or a mixture thereof (e.g. comprises a linear alkyl, a (poly)cyclic alkenyl and an aryl moiety).

Furthermore, according to any of the above-mentioned embodiments of the invention, said compound (I) is obtained in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives wherein the molar ratio between β–γ derivative and the α–β derivative (i.e. β–γ/α–β) is at least 4 or even at least 6. Of particular interest are the processes wherein said ratio is above 8 or even above 15.

Simultaneously or alternatively to the above-mentioned selectivity of the β–γ/α–β ratio, according to any of the above-mentioned embodiments of the invention, said compound (I) is obtained in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives as mentioned above and wherein the molar ratio of the isomers E and Z of the β–γ unsaturated derivatives ((E)- β–γ)/((Z)-β–γ) is above 1, or even above 2. Furthermore, said ratio (E)/(Z) of the β–γ unsaturated derivative of formula (I) can be above 3 or even 4, and in some cases can be increased in order to be above 5.

In particular one may cite an embodiment wherein the compound of formula (I) is obtained in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives wherein β–γ/α–β is at least 5.5, or even 15, and the ratio of the isomers ((E)-β–γ)/((Z)-β–γ) is above 3.5.

Non-limiting examples of compound of formula (I) are compounds of formula



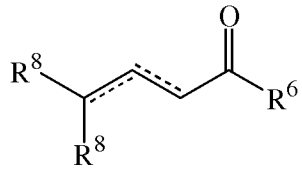
(V)

wherein R^6 represents a methyl or ethyl group or a OMe or OEt group; and

R^7 represents

- a C_{10-12} hydrocarbon group, such as a 2-(2,6,6-trimethyl-cyclohex-1-enyl)-ethyl group;
- a phenyl group optionally substituted with 1 or 2 C_1-C_3 alkoxy or amino groups; or
- a C_3-C_6 alkyl or alkenyl group.

Other examples of compound of formula (I) are



(VI)

wherein R^6 is as defined in formula (V) and the R^8 are taken together to form a C_4-C_{11} hydrocarbon group, such as:

- a $CH_2(CH_2)_nCH_2$ n representing 2, 3, 4 or 9;
- an unsaturated C_5-C_9 hydrocarbon group.

According to alternative embodiments of the invention, the process is particularly useful for the compounds of formula (I) which are esters or alternatively ketones.

According to an embodiment of the formulae (V) or (VI), the invention's process can be particularly useful when using as starting material the corresponding compounds of formula (II) wherein at least one R^6 is a OMe or OEt group, or even the two R^6 are both OMe or OEt groups.

As mentioned above, the invention's process is run in the presence of at least one compound from the group i) and at least one compound from the group ii), said groups consisting respectively of:

i) the salts of formula MX_2, $M''X_3$ or $M'X$, wherein M is an alkali-earth cation and M' an alkali cation or C_0-C_{12} ammonium cation and M" is a lanthanide cation, and X is a halide or an anion of an acid HX having a pK_a comprised between 0 and 6;
ii) the carboxylic acids of formula R^5COOH, wherein R^5 represents a C_1-C_{18} hydrocarbon group optionally comprising one or two oxygen atoms;

and optionally in the presence of a polar aprotic solvent having a boiling point of above 100°C.

According to an embodiment of the invention, the reaction is carried out in the presence of at least one compound from the group i) and at least one compound from the group ii):

i) the salts of formula MX_2 or $M''X_3$, wherein M is an alkali-earth cation and M' an alkali cation or C_0-C_{12} ammonium cation and M" is a lanthanide cation, and X is a halide or an anion of an acid HX having a pK_a comprised between 0 and 6; and

ii) an acid R^5COOH, wherein R^5 represents a C_1-C_{18} hydrocarbon group optionally comprising one or two oxygen atoms.

According to another embodiment of the invention, the compounds of group i) can be a magnesium, calcium, cerium, lithium, sodium or potassium salt of chloride, fluoride, iodine, or of a carboxylate of formula R^9COO^-, R^9 representing a C_1-C_{18} hydrocarbon group optionally comprising one or two oxygen atoms.

In particular one may cite the chloride and the carboxylates salts.

Non-limiting examples of such salts are NaCl, NaF, NaI, $Mg(R^9COO)_2$, R^9COONa, R^9COOK, KF, $CeCl_3$, $Ce(R^9COO)_3$, $CaCl_2$ and CaF_2. This salt can be formed in situ, prior to its use, by reacting together the metal oxide or hydroxide with the required amount of the acid HX.

According to a particular embodiment of the invention, R^9 represents a C_2-C_9 alkyl, alkenyl, phenyl or benzyl group. In particular one may cite groups such as pent-2-yl, hept-3yl, propyl, isopropyl, isobutyl, tertbutyl, isopentyl, cyclohexyl, benzyl or $(Me)_2(CH_2)_3C(Me)=CH$.

In the case wherein the compound of formula (I) is an ester, the corresponding carboxylate can also be used.

According to an embodiment of the invention, the compounds of group ii) can be a carboxylic acid R^9COOH, wherein R^9 is as defined above.

According to an embodiment of the invention, the polar aprotic solvent can be a solvent having a boiling point of above 120°C. Furthermore it can be selected from the group consisting of a C_2-C_6 dialkyl sulfoxide, a C_2-C_6 dialkyl sulfone, a C_3-C_7 amide or lactam, a C_3-C_8 urea or pyrimidone derivative, C_6-C_{12} phosphoramide or phosphino-amino derivative, a C_3-C_8 nitriles, a C_4-C_8 mono or diethylene glycol di-ether, and triethanolamine.

In particular one may cite the following: DMSO, NMP (N-methyl pyrrolidone), DMF, HMPA, DMPU or diglyme.

The various compounds of the groups i) to iii) can be added to the reaction medium in a large range of concentrations. As non-limiting examples, one can cite as group i) concentration ranging from 0.5 % to 200%, relative to the molar amount of the compound (II). Preferably, the group i) concentration will be comprised between 1 % to 30%.

As non-limiting examples, one can cite as group ii) concentration ranging from 0.0 % to 300%, relative to the molar amount of the compound (II). Preferably, the group ii) concentration will be comprised between 60 % to 220%.

As non-limiting examples, one can cite as group iii) concentration ranging from 0.0% to 500%, relative to the weight of the compound (II). Preferably, the group iii) concentration will be comprised between 0.0 % to 300%.

It goes without saying that the optimum concentrations of each compound of the various list will depend on the nature of the latter and of the compound (II).

The temperature at which the hydrogenation can be carried out is comprised between 100°C and 230°C, more preferably in the range of between 120°C and 190° C. Of course, a person skilled in the art is also able to select the preferred temperature as a function of the melting and boiling point of the starting and final products and of the desired speed of reaction.

The starting compounds (II) can be prepared according the standard method known by the person skilled in the art, and as also described in the examples. They may also be prepared in situ, also as described in the examples.

The invention will now be described in further detail by way of the following examples, wherein the temperatures are indicated in degrees centigrade and the abbreviations have the usual meaning in the art.

Examples

All the procedures described hereafter have been carried out under an inert atmosphere unless stated otherwise. All substrates and solvents were distilled from appropriate drying agents under Ar.

Example 1

A) General procedure

The starting compound (II) (obtained according to the literature) (0.24 mol) (see Table 4) was heated at 160°C for 10- 9h, in the presence of Mg(2-ethyl hexanate) (0.045moles) and 2-ethyl hexanoic acid (0.24 mol).After cooling at 50°C, the mixture is washed with 10g H_2SO_4 20%, and distilled in vacuo to give the unsaturated esters. Table 4 gives the yields and the various isomers of compound (I).

Table 4

Compound (II)	Compound (I)	Yield (%)	The ratio of the isomers
$PhCHMeCH=C(COOMe)_2$	Methyl 4-phenyl-3-pentenoate	80	β–γ/α–β = 49 (E)-β–γ /(Z)-β–γ = 5.3/1
Dimethyl [2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)butylidene]malonate	Methyl 4-methyl-6-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-hexenoate	90	β–γ/α–β = 49 (E)-β–γ /(Z)-β–γ = 5.1/1

B) General procedure

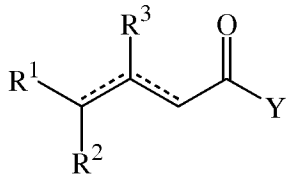
Same experimental procedure as above, using as starting compound dimethyl [2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)butylidene]malonate and varying the catalyst. Results showed in Table 5.

Table 5 : 2-EH = 2-ethyl hexanoate

Catalyst	Acid	Conversion	The ratio of the isomers
$MgCl_2$	Propionic	96	β–γ/α–β = 28 (E)-β–γ /(Z)-β–γ = 4.7
CeCl3	Propionic	100	β–γ/α–β = 18 (E)-β–γ /(Z)-β–γ = 5.1
LiCl	Propionic	95	β–γ/α–β = 8 (E)-β–γ /(Z)-β–γ = 4.8
$Mg(2\text{-}EH)_2$	2-ethyl hexanoic	98	β–γ/α–β = 48 (E)-β–γ /(Z)-β–γ = 5.1
$Ca(2\text{-}EH)_2$	2-ethyl hexanoic	85	β–γ/α–β = 17 (E)-β–γ /(Z)-β–γ = 8

Claims

1. A process for the preparation of a compound of formula (I)



(I)

wherein the dotted lines indicate that the compound is in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives, the molar ratio β–γ/α–β being at least 3;

Y represent, independently of each other, a OR^4 or R^4 group, R^4 representing a C_1-C_8 hydrocarbon group, optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

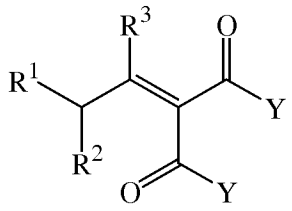
R^1 represents a C_1-C_{15} hydrocarbon group, optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

R^2 represents a C_1-C_5 hydrocarbon group, optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

R^3 represents a hydrogen atom or a C_1-C_5 hydrocarbon group; and

optionally said R_1 and R_2, and/or R_1 and R_3, taken together may form a C_4-C_{12} hydrocarbon group optionally comprising 1 to 3 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen;

said method comprising the step of reacting, at a temperature comprised between 100°C and 230°C, a compound of formula



(II)

wherein Y, R^1, R^2 and R^3 are defined as in formula (I);

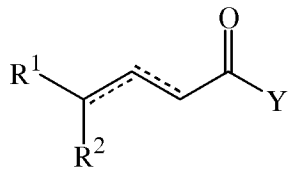
with at least one compound from the group i) and at least one compound from the group ii), said groups consisting respectively of:

i) the salts of formula MX_2, $M''X_3$ or $M'X$, wherein M is an alkali-earth cation and M' an alkali cation or C_0-C_{12} ammonium cation and M" is a lanthanide cation, and X is a halide or an anion of an acid HX having a pK_a comprised between 0 and 6;

ii) the carboxylic acids of formula R^5COOH, wherein R^5 represents a C_1-C_{18} hydrocarbon group optionally comprising one or two oxygen atoms;

and optionally in the presence of a polar aprotic solvent having a boiling point of above 100°C.

2. A process according to claim 1, characterised in that the compound of formula (I) is of formula



(III)

the dotted lines indicate that the compound is in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives, the molar ratio β–γ/α–β being at least 3;

Y represent, independently of each other, a OR^4 or R^4 group, R^4 representing a C_1-C_6 alkyl group or a C_6-C_{10} phenyl or benzyl group optionally comprising 1 to 3 oxygen or nitrogen atoms;

R^1 represents a C_2-C_{12} hydrocarbon atom, optionally comprising 1 to 3 functional oxygen or nitrogen atoms;

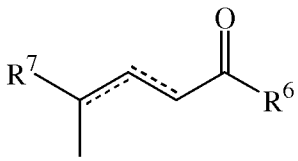
R^2 represents a C_1-C_3 alkyl group;

optionally said R_1 and R_2, taken together may form a C_4-C_{11} hydrocarbon group optionally comprising 1 to 3 oxygen or nitrogen atoms.

3. A process according to claim 1, characterised in that said compound (I) is obtained in the form of a mixture of the corresponding β–γ or α–β unsaturated derivatives and wherein the ratio β–γ/α–β is at least 6; and/or

the molar ratio of the isomers E and Z of the β–γ unsaturated derivatives, (E)- β–γ)/((Z)-β–γ, is above 3.

4. A process according to claim 1, characterised in that the compounds of formula (I) are compounds of formula



(V)

wherein R^6 represents a methyl or ethyl group or a OMe or OEt group; and

R^7 represents

- a C_{10-12} hydrocarbon group;
- a phenyl group optionally substituted with 1 or 2 C_1-C_3 alkoxy or amino groups; or
- a C_3-C_6 alkyl or alkenyl group.

5. A process according to claim 1, characterised in that the compound of formula (II) is reacted with in the presence of at least one compound from the group i) and at least one compound from the group ii):

i) the salts of formula MX_2, $M''X_3$ or M'X, wherein M is an alkali-earth cation and M' an alkali cation or C_0-C_{12} ammonium cation and M" is a lanthanide cation, and X is a halide or an anion of an acid HX having a pK_a comprised between 0 and 6, in particular a MX_2 or $M''X_3$ salt; and

ii) an acid R^5COOH, wherein R^5 represents a C_1-C_{18} hydrocarbon group optionally comprising one or two oxygen atoms.

6. A process according to claim 5, characterised in that the compounds of group i) are the salts of formula MX_2 or $M''X_3$, wherein M, M" and X are as defined in claim 5.

7. A process according to claim 5, characterised in that the compound of group i) is a magnesium, calcium, cerium, lithium, sodium or potassium salt of chloride,

fluoride, iodine, or of a carboxylate of formula R^9COO^-, R^9 representing a C_1-C_{18} hydrocarbon group optionally comprising one or two oxygen atoms.

8. A process according to claim 7 characterised in that the salt is NaCl, NaF, NaI, $Mg(R^9COO)_2$, R^9COONa, R^9COOK, KF, $CeCl_3$, $Ce(R^9COO)_3$, $CaCl_2$ or CaF_2, R^9 being defined as in claim 7.

9. A process according to claim 1, characterised in that the compound of group ii) is a carboxylic acid R^9COOH, wherein R^9 is a C_2-C_9 alkyl, alkenyl, phenyl or benzyl group.

10. A process according to claim 9, characterised in that R^9 represents a pent-2-yl, hept-3yl, propyl, isopropyl, isobutyl, tertbutyl, isopentyl, cyclohexyl, benzyl or $(Me)_2(CH_2)_3C(Me)=CH$ group.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/050341

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C67/32 C07C69/618 C07C403/20

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

B. FIELDS SEARCHED

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SCHULTE-ELTE, KARL H.; PAMINGLE, HERVE; UIJTTEWAAL, ARNOLD P.; SNOWDEN, ROGER L.: "An alternative access to (.+-.)-.alpha.-irones and (.+-.)-.beta.-irone via acid-mediated cyclization." HELVETICA CHIMICA ACTA., vol. 75, 1992, pages 759-765, XP002393151 VERLAG HELVETICA CHIMICA ACTA, BASEL., CH cited in the application page 759 page 761; figure 1 page 763, paragraphs 1,2	1

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

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
5 June 2007	13/06/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kardinal, Siegmar

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KRAPCHO A P: "SYNTHETIC APPLICATIONS OF DEALKOXYCARBONYLATIONS OF MALONATE ESTERS, BETA-KETO ESTERS, ALPHA-CYANO ESTERS AND RELATED COMPOUNDS IN DIPOLAR APROTIC MEDIA - PART I" SYNTHESIS, GEORG THIEME VERLAG, STUTTGART, DE, October 1982 (1982-10), pages 805-822, XP000999104 ISSN: 0039-7881 the whole document	1
A	KRAPCHO A P: "SYNTHETIC APPLICATIONS OF DEALKOXYCARBONYLATIONS OF MALONATE ESTERS, BETA-KETO ESTERS, ALPHA-CYANO ESTERS AND RELATED COMPOUNDS IN DIPOLAR APROTIC MEDIA - PART II" SYNTHESIS, GEORG THIEME VERLAG, STUTTGART, DE, November 1982 (1982-11), pages 893-914, XP000999105 ISSN: 0039-7881 the whole document	1
A	A. P. KRAPCHO ET AL.: "Synthetic Applications and Mechanism Studies of the Decarboxylations of Geminal Diesters and Related Systems Effected in Me2SO by Water and/or by Water with Added Salts" JOURNAL OF ORGANIC CHEMISTRY., vol. 43, no. 1, 1978, pages 138-146, XP002393152 AMERICAN CHEMICAL SOCIETY. EASTON., US the whole document	1
A	A. H. DICKINS ET AL.: "The Chemistry of Three-carbon System. Part XX. cyclo-Pentylideneacetone and cyclo-Pentylidenemethyl Ethyl Ketone." JOURNAL OF THE CHEMICAL SOCIETY., 1929, pages 571-580, XP008067320 GBCHEMICAL SOCIETY. LETCHWORTH. page 576, line 3 - line 8	1
A	RAGOUSSIS ET AL: "Palladium catalyzed reductive decarboxylation of allyl alpha-alkenyl-beta-ketoesters. A new synthesis of (E)-3-alkenones" TETRAHEDRON LETTERS, ELSEVIER, AMSTERDAM, NL, vol. 47, no. 5, 30 January 2006 (2006-01-30), pages 683-687, XP005222409 ISSN: 0040-4039 * page 684, table 1, entries b and d *	1