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(54) **METHOD OF PRODUCING DIOL, POLYDIOL, SECONDARY ALCOHOL OR DIKETONE COMPOUND**

VERFAHREN ZUR HERSTELLUNG EINER DIOL-, POLYDIOL-, SEKUNDÄRALKOHOL- ODER DIKETON-VERBINDUNG

PROCÉDÉ DE PRODUCTION DE COMPOSÉ DIOL, POLYDIOL, ALCOOL SECONDAIRE OU DICÉTONE

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WO-A1-03/089373 **WO-A1-2005/000741**
JP-A- 04 300 971 **JP-A- 2002 265 391**
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EP 2 067 761 B1

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- HAGINIWA J ET AL: "Reactions Concerned in Tertiary Amine N-Oxides. XV. Dimerization Reactions of Anthrone and Its Derivatives Using Pyridine N-Oxide as Oxidizing Reagent", YAKUGAKU ZASSHI - JOURNAL OF THE PHARMACEUTICAL SOCIETY OF JAPAN, JAPAN SCIENCE AND TECHNOLOGY INFORMATION AGGREGATOR, ELECTRONIC, JP, vol. 103, no. 3, 1 January 1983 (1983-01-01), pages 273-278, XP003021747, ISSN: 0031-6903
- HAGINIWA J. ET AL.: 'Reactions Concerned in Tertiary Amine N-Oxides. XV. Dimerization Reactions of Anthrone and Its Derivatives Using Pyridine N-Oxide as Oxidizing Reagent' vol. 103, no. 3, 1983, pages 273 - 278, XP003021747
- DATABASE CAPLUS [Online] XU J.H. ET AL.: 'Photoinduces reductions of chalcone derivatives in the presence of amines', XP003021748 Database accession no. (1996: 424552) & JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY, A: CHEMISTRY vol. 97, no. 1-2, 1996, pages 33 - 43
- BUCHAMMAGARI H. ET AL.: 'Room Temperature-Stable Electride as a Synthetic Organic Reagent: Application to Pinacol Coupling Reaction in Aqueous Media' ORGANIC LETTERS vol. 9, no. 21, 2007, pages 4287 - 4289, XP003021749

Description

Technical Field

5 **[0001]** The present invention relates to a process for producing a diol or polydiol, or a secondary alcohol or diketone compound by use of an $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride as a reducing agent.

Background Art

10 **[0002]** About the synthesis of a diol by reductive coupling reaction of a carbonyl compound, it is known that a metal compound or metal salt, such as magnesium amalgam, aluminum amalgam, samarium iodide or vanadium chloride, functions as a reducing agent (Non-Patent Document 1).

15 **[0003]** However, the metal compound or metal salt is expensive and harmful, and further it is necessary to conduct the reaction in a water-free organic solvent in the atmosphere of an inert gas. For this reason, the reaction using the metal compound or metal salt was very unsatisfactory for a simple and environment-friendly reducing process. Known is also a process of conducting the reaction in an organic solvent, using metallic calcium as a reducing agent (Patent Document 1).

20 **[0004]** Secondary alcohols and diketones containing an aryl group and/or an alkyl group are widely used as intermediate compounds for medical supplies, colorants, and others. It is necessary to synthesize these compounds by an environment-friendly and safe process.

25 **[0005]** For the synthesis of a secondary alcohol through reductive reaction of a ketone compound, it is known that a metal hydride containing boron or aluminum, such as NaBH_4 , LiBH_4 , LiAlH_4 or $\text{Zn}(\text{BH}_4)_2$, functions as a reducing agent. However, the metal hydride is expensive and harmful, and further these metal hydride has a drawback that the metal hydride can be used only in a dry atmosphere and a dry solvent containing no water since the metal hydride dislikes the presence of water extremely. Besides, known is a process of causing polymethylhydrosiloxane to react with a ketone in the presence of a catalytic amount of tetrabutylammonium fluoride to reduce the carbonyl group of the ketone, thereby yielding an alcohol compound (Patent Document 2).

30 **[0006]** In 1970, H. B. Bartl et al. disclosed that the crystal of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (referred to as "C12A7") has a unique crystal structure that two out of 66 oxygen ions present in a cell containing two molecules thereof undergo clathration, as "free oxygen", into spaces in cages present in the crystal (Non-Patent Document 2). Thereafter, it was made evident that the free oxygen ions can be substituted with various anions. In particular, when C12A7 is held in an intensely reducing atmosphere, entire free oxygen can be substituted with electrons. C12A7:e^- , wherein free oxygen is substituted with electrons, can be regarded as an electride.

35 **[0007]** Electride compounds are based on an idea suggested unprecedentedly by J. L. Dye (Non-Patent Document 3). No electride compounds were realized until a compound containing a crown ether as a cation and an electron as an anion, and other compounds were produced. It is known that an electride exhibits electroconductivity through the hopping of an electron contained as an anion. Thereafter, some organic electriles were found out. However, all of these compounds are stable only at a temperature as low as about -100°C or lower, and are remarkably unstable compounds reactive with air or water.

40 **[0008]** The inventors filed, as a patent application, an invention relating to electroconductive C12A7 and analogue compounds thereof, and a production process thereof (Patent Document 3). The inventors found out that a C12A7 compound having an electroconductivity of 10^3 S/cm or less is yielded by annealing C12A7 monocrystal at high temperature in a vapor of an alkali metal or alkaline earth metal, ion-implanting an inactive ion such as Ar into C12A7 monocrystal, or solidifying C12A7 monocrystal directly from a melt in a reducing atmosphere. An invention relating thereto was filed as a patent application (Patent Document 4). Furthermore, the inventors succeeded in yielding C12A7 exhibiting metallic electroconductivity by annealing C12A7 monocrystal in a vapor of metallic titanium (Ti), and then filed, as a patent application, the production process of C12A7, and a usage thereof as an electron-releasing material (Patent Document 5).

45 **[0009]** These C12A7 compounds, which exhibit a good electroconductivity, are compounds wherein all of free oxygen ions are substituted with electrons, are each substantially represented by $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4\text{e}^-)$, and can be regarded as inorganic electride compounds (Non-Patent Document 4).

50 **[0010]** Electrons undergoing clathration into C12A7 electriles are loosely bonded to cations, so that the electrons can be taken into the outside by applying an electric field thereto or by a chemical means. It appears that the electrons taken into the outside can be used in reductive reaction. However, unknown is an example in which electrons undergoing clathration into a C12A7 electride are applied directly to reductive reaction.

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Non-Patent Document 1: G. M. Robertson, Comprehensive Organic Synthesis 3, 563 (1991)

Non-Patent Document 2: H. B. Bartl, T. Scheller and N. Jarhrb, Mineral Monatsh, 1970, 35, 547-552

EP 2 067 761 B1

Non-Patent Document 3: F. J. Tehan, B. L. Barrett, J. L. Dye, J. Am. Chem. Society, 96, 7203-7208 (1974)

Non-Patent Document 4: S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka and H. Hosono, Science, 301, 626-629 (2003)

Patent Document 1: Japanese Patent Application Laid-Open (JP-A) No. 2002-265391

Patent Document 2: JP-A No. 10-87530

Patent Document 3: WO 2005/000741A1

Patent Document 4: JP-A No. 2004-26608

Patent Document 5: WO 2007/060890A1

[0011] EP 1 215 173 discloses a C12A7 compound which clathrates active oxygen species in a high concentration and allows the clathrated active oxygen species or oxygen ions to be released at a high temperature of 1250°C or more.

[0012] EP 1 445 237 A1 discloses that C12A7 can reversibly clathrate or release On ion radicals through the elevation or lowering of the temperature in a range of 300 to 850°C.

[0013] WO 03/089373 A1 and WO 2005/000741 A1 disclose C12A7 as being a material which is capable of exhibiting a function of being converted from an insulative material to an electrically conductive material in a sustained manner.

[0014] JP 2002-332252 discloses a method for producing optically active benzhydrols, comprising a step for reacting asymmetric benzophenones with a boron hydride metal compound.

[0015] Haginiwa et al. (Yakugaku Zasshi - Journal of the Pharmaceutical Society of Japan 103(3): 273-278 (1983)) discloses a method for producing inter alia dianthrone.

Disclosure of the Invention

Problems to be solved by the invention

[0016] An object of the invention is to provide a novel reductive reaction for synthesizing a diol or polydiol by use of a carbonyl compound as a raw material or synthesizing a secondary alcohol or diketone compound by use of a ketone compound as a raw material without using an expensive and harmful metal hydride or metal salt for the synthesizing reaction nor limiting the atmosphere for the reaction to an inert gas atmosphere as in conventional processes.

Means for solving the problems

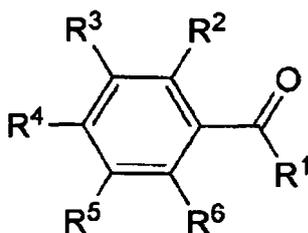
[0017] In order to attain the object, the inventors have been repeatedly made eager investigations, so as to find out that when a C12A7 electride, which exhibits electroconductivity, is used as a reducing agent, a reductive coupling reaction of a carbonyl compound or a reductive reaction of a ketone compound advances in water, an organic solvent, or a water/organic mixed solvent under the air also.

[0018] Accordingly, the invention is (1) a process for producing a diol or polydiol, as defined in the claims comprising the step of using, as a reducing agent, a $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride containing electrons in a number of 10^{19} cm^{-3} or more and $2.3 \times 10^{21}\text{ cm}^{-3}$ or less in its cages to subject a carbonyl compound to reductive coupling in water, an organic solvent, or a mixed solvent of water and an organic solvent.

[0019] The invention is also (2) the process for producing a diol or polydiol according to item (1), wherein the carbonyl compound is a compound wherein at least one out of two substituents bonded to a carbonyl group is an aryl group.

[0020] The invention is also (3) the process for producing a diol or polydiol according to item (1), wherein the carbonyl compound is represented by the following general formula:

[Chemical formula 1]



wherein R¹ is a functional group selected from a hydrogen atom, an alkyl group and an aryl group, R², R³, R⁴, R⁵ and

R⁶ are each a functional group, bonded to the aryl group, selected from a hydrogen atom, a chloro group, a bromo group, an iodo group, an alkyl group, an aryl group, a carbonyl group, an allyl group, a vinyl group, an amino group, a hydroxy group, an alkoxy group, a nitro group, a cyano group, and an imino group, and R¹ and the aryl group may be bonded to each other to form a ring structure.

[0021] The invention is also (4) the process for producing a diol or polydiol according to item (1), wherein about the use amount of the 12CaO·7Al₂O₃ electrone relative to the carbonyl compound (12CaO·7Al₂O₃/the carbonyl compound), the ratio by weight of the former to the latter is from 2 to 20.

[0022] The invention is also (5) the process for producing a diol or polydiol according to item (1), wherein a reaction atmosphere for the reductive coupling is in the air. [Definition of Carbonyl Compound]

[0023] In the invention, a carbonyl compound is defined as a compound wherein two substituents are bonded to a carbonyl group and the two substituents are each one selected from an alkyl group, an aryl group, and hydrogen. However, the compound wherein the two substituents are simultaneously hydrogen is not included therein.

[Definition of Diol]

[0024] In the invention, a diol is defined as a compound wherein a hydroxy group is bonded to each of two carbon atoms adjacent to each other. A polydiol is defined as a compound containing this diol structure and one or more diol structures equal thereto.

[0025] Furthermore, the invention is (6) a process for producing a secondary alcohol, as defined in the claims, comprising the step of using, as a reducing agent, a 12CaO·7Al₂O₃ electrone containing electrons in a number of 10¹⁹ cm⁻³ or more and 2.3 × 10²¹ cm⁻³ or less in its cages to reduce a ketone compound represented by the formula of compound 1 in the following reaction equation 1 in water, an organic solvent, or a mixed solvent of water and an organic solvent, thereby synthesizing the secondary alcohol which is a secondary alcohol represented by the formula of compound 2 in the reaction equation 1:

(reaction equation 1)

[Chemical formula 2]



(compound 1: ketone)

(compound 2: secondary alcohol)

wherein R and R¹ are functional group selected from an aryl group and an alkyl group, and at least one of R and R¹ contains an aryl group.

[0026] The invention is also (7) a process for producing a dianthrone, as defined in the claims, comprising the step of using, as a reducing agent, a 12CaO·7Al₂O₃ electrone containing electrons in a number of 10¹⁹ cm⁻³ or more and 2.3 × 10²¹ cm⁻³ or less in its cages to dimerize an arylketone compound (anthrone) represented by the formula of compound 3 in the following reaction equation 2 in a mixed solvent of water and an organic solvent, thereby synthesizing the dianthrone which is a dianthrone represented by the formula of compound 4 in the reaction equation 2:

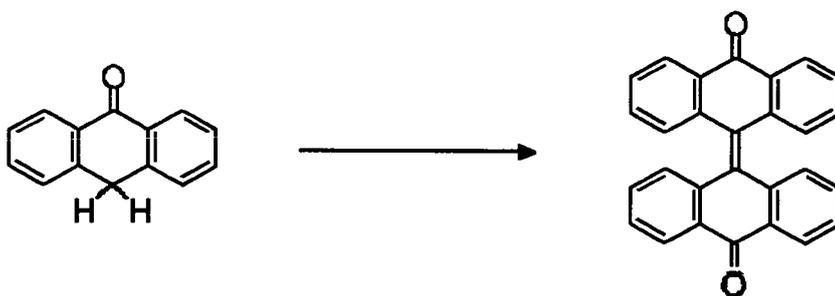
(reaction equation 2)

[Chemical formula 3]

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(compound 3: anthrone)

(compound 4: dianthrone)

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[0027] Additionally, the invention is (8) a process for producing a dichalcone mixture, as defined in the claims, comprising the step of using, as a reducing agent, a $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride containing electrons in a number of 10^{19} cm^{-3} or more and $2.3 \times 10^{21}\text{ cm}^{-3}$ or less in its cages to dimerize a ketone compound represented by the formula of compound 5 in the following reaction equation 3 (chalcone), which contains a carbon double bond, in a mixed solvent of water and an organic solvent, thereby synthesizing dichalcones represented by the formulae of compound 6 and compound 7 in the reaction equation 3:

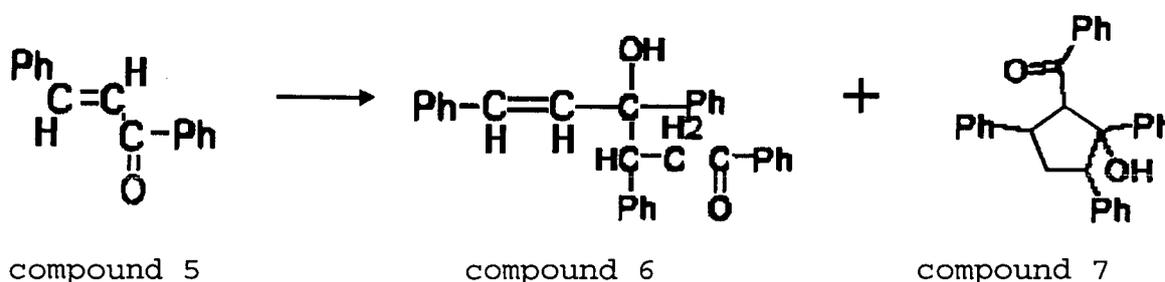
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(reaction equation 3)

[Chemical formula 4]

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compound 5

compound 6

compound 7

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[Definition of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) Electride]

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[0028] In the crystal structure of C12A7, 12 cages are present per its cell, which is composed of two molecules thereof, and oxygen ions (O^{2-}) undergo clathration into two of the cages. The oxygen ions can partially or wholly be substituted with electrons. When the oxygen ions are wholly substituted, the electron concentration is $2.3 \times 10^{21}\text{ cm}^{-3}$. In the invention, a compound wherein oxygen ions undergoing clathration therein are partially substituted with electrons (in a number of $1 \times 10^{19}\text{ cm}^{-3}$ or more and $2.3 \times 10^{21}\text{ cm}^{-3}$ or less), or are wholly substituted therewith (in a number of $2.3 \times 10^{21}\text{ cm}^{-3}$) is defined as a C12A7 electride (C12A7:e⁻).

50

[0029] A C12A7 electride can be obtained by annealing C12A7 having a stoichiometric composition at about 700°C in a metallic Ca vapor or annealing C12A7 having a stoichiometric composition at about 1100°C in a metallic Ti vapor. The electron concentration in C12A7 becomes larger in accordance with the increase in annealing time.

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[0030] In the case of treating in the metallic Ti vapor, a C12A7 electride having a theoretical maximum electron concentration ($2.3 \times 10^{21}\text{ cm}^{-3}$) can be obtained by the annealing for about 24 hours, even if C12A7 is monocrystal of 3 mm thickness. Also a C12A7 melt having a stoichiometric composition may be solidified in a reducing atmosphere. The concentration of the C12A7 electride obtained by the solidification in the reducing atmosphere is 10^{21} cm^{-3} or less. A C12A7 electride can be prepared also by ion-implanting Ar^+ ions into a high concentration in C12A7. The electron concentration in the resultant C12A7 electride can be obtained based on the intensity of the optical band, which has a peak at 2.8 eV. When the electron concentration is small, the electron concentration can be obtained also based on the

intensity of the electron spin resonance absorption band.

Advantageous effects of the invention

5 **[0031]** According to the process of the invention, as defined in the claims, it is possible to synthesize a diol or polydiol from a carbonyl compound as a raw material or synthesize a secondary alcohol or diketone compound from a ketone compound as a raw material through simple operations in a short period without using an expensive and harmful metal hydride or metal salt for the synthesizing reaction nor limiting the atmosphere for the reaction to an inert gas atmosphere as in conventional processes.

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Best Mode for Carrying Out the Invention

[0032] A C12A7 electride used as a reducing agent may be in the form of powder, a solid sintered body or a solid crystal, or in any other form. About the powdery C12A7 electride, it is advisable to anneal C12A7 powder having a stoichiometric composition in a metallic Ca vapor or a metallic Ti vapor. About the C12A7 electride in the form of a solid sintered body, it is advisable to solidify a C12A7 melt having a stoichiometric composition in a reducing atmosphere. About the C12A7 electride in the form of a solid monocrystal, it is advisable to anneal a C12A7 monocrystal in a metallic Ca vapor or a metallic Ti vapor. In order to make the reductive reaction rate larger, it is most suitable to convert a solid sample into powder. For the powdering process, pulverization in a mortar, pulverization by use of a jet mill, or the like may be used.

20

<Process for Reducing Carbonyl Compound>

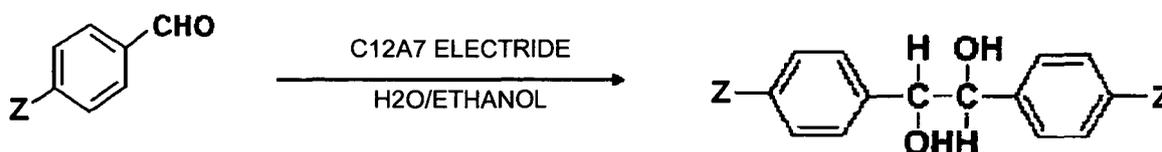
[0033] The carbonyl-compound-reducing process of the invention will be described in detail hereinafter.

25 **[0034]** The carbonyl-compound-reducing process of the invention is a process of using, as a reducing agent, a $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride containing electrons in a number of 10^{19} cm^{-3} or more and $2.3 \times 10^{21}\text{ cm}^{-3}$ or less in its cages to subject a carbonyl compound to reductive coupling in a solvent. In using, for example, benzaldehyde as the carbonyl compound, 1,2-diphenyl-1,2-ethanediol can be produced by a reductive coupling reaction by the following equation:

30

[Chemical formula 5]

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[0035] The invention as defined in the claims can be applied to a carbonyl compound. Example of the carbonyl compound represented by the general formula illustrated above include 1-naphthoaldehyde, 2-naphthoaldehyde, 1-bromo-2-naphthoaldehyde, 2-hydroxy-1-naphthoaldehyde, 1-hydroxy-2-naphthoaldehyde, 2-methoxy-1-naphthoaldehyde, 1-methoxy-2-naphthoaldehyde, 6-methoxy-2-naphthoaldehyde, 1-nitro-2-naphthoaldehyde, 2,3-dimethoxy-1-naphthoaldehyde, 4-hydroxy-1-naphthoaldehyde, and 2,3-naphthalenedialdehyde, or the like.

45

[0036] Examples of a compound wherein R^1 is H out of the carbonyl compounds represented by the general formula illustrated above include benzaldehyde, 4-methylbenzaldehyde, 4-ethylbenzaldehyde, 4-t-butylbenzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, 2-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-hydroxybenzaldehyde, 4-cyanobenzaldehyde, 4-ethoxycarbonylbenzaldehyde, 2,4-dimethoxybenzaldehyde, 4-bromobenzaldehyde, 4-octyloxybenzaldehyde, 4-dimethylaminobenzaldehyde, and 2-hydroxybenzaldehyde, or the like.

50

[0037] As the solvent, the following may be used: water; an organic solvent, such as an alcohol such as methanol, ethanol or propanol, an ether such as tetrahydrofuran, dioxane or diethyl ether, chloroform, methylene chloride, benzene, toluene, N,N-dimethylformamide, or dimethylsulfoxide; a mixed organic solvent of two or more thereof; or a water/organic mixed solvent. From the viewpoint of the environment, only water or an organic mixed solvent containing water is most preferred. If the ratio by volume of the organic solvent (organic solvent/ (water + organic solvent)) becomes larger, the reaction rate becomes smaller. The ratio is desirably 0 or more and less than 80.

55

[0038] About the use amount of the C12A7 electride relative to the carbonyl compound (C12A7/the carbonyl compound), the ratio by weight of the former to the latter is preferably from 2 to 20. If the ratio is less than 2, the reaction rate is small. If the ratio is 20 or more, the viscosity of the solution increases so that the solution is not easily stirred smoothly.

[0039] The atmosphere for the reaction is preferably the atmosphere of air having a pressure of 1 atm., and may be

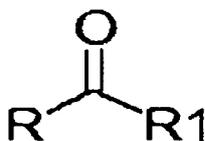
an inactive atmosphere. As the reaction temperature rises, the reaction rate increases. Practically, the temperature is most desirably room temperature. The temperature preferably ranges from 0°C to 100°C. If the temperature is 0°C or lower, water unfavorably freezes. If the temperature is 100°C, water unfavorably vaporizes so that the reaction does not advance. The reaction time depends on the kind of the carbonyl compound and the reaction temperature; however, the reaction ends completely in a time from 15 hours to 96 hours.

[0040] Under conditions as described above, the carbonyl compound and C12A7 are stirred and mixed in the solvent. Next, a product is extracted from the reaction solution in post-treatment. The method for the extraction may be a known method adopted as a method of extraction from a reaction solution. Specifically, for example, hydrochloric acid is added to the reaction solution, and then, for example, ethyl acetate is added thereto so as to extract the product. This extracting process is repeated about 3 times, and then the product is washed with sodium bicarbonate solution and sodium chloride solution. Thereto is added magnesium sulfate to dry the solution. Thereafter, magnesium sulfate is filtrated off, and the solvent is distilled off. The resultant is purified by column chromatography (silica gel). The finally produced compound can be separated by the chemical pre-treatment and the column chromatography. The identification of the compound and the rate of the conversion from the starting material can be obtained based on the H¹ nuclear magnetic resonance spectrum.

<Process for Reducing Ketone Compound>

[0041] The ketone-compound-reducing process of the invention will be described in detail hereinafter. The ketone-compound-reducing process of the invention as defined in the claims is a process of using, as a reducing agent, a 12CaO·7Al₂O₃ electride containing electrons in a number of 10¹⁹ cm⁻³ or more and 2.3 × 10²¹ cm⁻³ or less in its cages to convert the carbonyl group C=O of a ketone compound to CH-OH in water, an organic solvent, or a mixed solvent of water and an organic solvent, thereby synthesizing a secondary alcohol. As the ketone compound, a compound 1 represented by the following formula is used:

[Chemical formula 6]



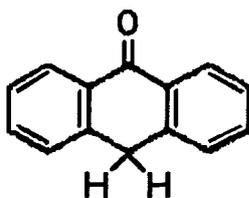
(compound 1: ketone)

R and R¹ are functional group selected from an aryl group and an alkyl group, and at least one of R and R¹ contains an aryl group. Preferably, R and R¹ are each one selected from a methyl group, a phenyl group, a phenylcyano group, or a phenylmethoxy group. However, a ketone compound wherein R and R¹ are simultaneously methyl groups is excluded. Specific examples thereof include p-cyanophenyl methyl ketone, di p-methoxyphenyl ketone, and diphenyl ketone, or the like. In the case of using, for example, p-cyanophenyl methyl ketone as the ketone compound, p-cyanophenyl methyl alcohol can be produced through reductive reaction.

[0042] The invention is also a process of using, as a reducing agent, a 12CaO·7Al₂O₃ electride containing electrons in a number of 10¹⁹ cm⁻³ or more and 2.3 × 10²¹ cm⁻³ or less in its cages to dimerize a ketone compound containing, besides the ketone group thereof, a different active group (such as a carbon double bond) in a solvent, thereby synthesizing a diketone, as defined in the claims.

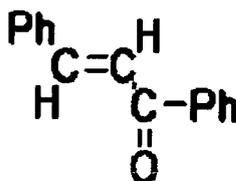
[0043] As the ketone compound containing, besides the ketone group, a different active group, the following is used: an aryl ketone compound 3 represented by a formula illustrated below (anthrone; 9,10-dihydroanthracene-9-one), or a ketone compound 5 containing a carbon double bond (chalcone; benzylideneacetophenone). In the case of using anthrone or chalcone as the active-group-containing ketone compound, dianthrone or dichalcone can be produced.

[Chemical formula 7]



compound 3 (anthrone)

[Chemical formula 8]



compound 5

[0044] For an easily-reducible ketone compound, about 50% of electrons in C12A7 are used in the reductive reaction thereof. Therefore, a C12A7 electrone having a higher electron concentration is more desirable. However, even an electrone having a small electron concentration can cause a reductive reaction of a ketone when the charging amount thereof is increased. The electron concentration is from 10^{19} cm^{-3} to $2.3 \times 10^{21} \text{ cm}^{-3}$, and is more preferably from 10^{20} cm^{-3} to $2.3 \times 10^{21} \text{ cm}^{-3}$. The electron concentration of a C12A7 electrone obtained directly by solidifying a melt in a reducing atmosphere is 10^{19} cm^{-3} or more. This low-electron-concentration electrone is also effective as a ketone-reducing agent.

[0045] In the production reaction of a secondary alcohol based on the reduction of a ketone, the following may be used as a solvent: water; an organic solvent, such as an alcohol such as methanol, ethanol or propanol, an ether such as tetrahydrofuran (THF), dioxane or diethyl ether, chloroform, methylene chloride, benzene, toluene, N,N-dimethylformamide, or dimethylsulfoxide; a mixed organic solvent of two or more thereof; or a mixed solvent of water and an organic solvent. From the viewpoint of the environment, only water or a mixed solvent of an organic solvent that contains water is preferred. If the ratio by volume of the organic solvent (organic solvent/(water + organic solvent)) becomes larger, the reductive reaction rate becomes smaller. The ratio is desirably 0 or more and 80 or less.

[0046] In the meantime, about the dimerization reaction of a ketone compound, the reaction does not advance in a solvent made only of water. Thus, a mixed solvent of water and an organic solvent are used. As the organic solvent, can be used CH_3CN , Et-OH, t-Bu-OH, dioxane, tetrahydrofuran (THF), or the like. In the dimerization reaction of anthrone, CH_3CN is suitable since no byproduct is generated. In the dimerization reaction of chalcone, tetrahydrofuran (THF) is suitable since the yield is high.

[0047] In any one of the reductive reaction and the dimerization reaction of a ketone, about the use amount of the C12A7 electrone relative to the ketone compound (C12A7/the ketone compound), the ratio by weight of the former to the latter is preferably from about 2 to 20. If the ratio is less than 2, the reductive reaction rate becomes small. If the ratio is more than 20, the viscosity of the solution increases so that the solution is not easily stirred smoothly. The ratio is more preferably from about 5 to 15. In the ketone-compound-reducing process of the invention, as defined in the claims, a catalyst is not particularly required since electrons contained in the C12A7 electrone are released in the reductive reaction so that the electrons react with a ketone compound.

[0048] The pressure in the reductive reaction may be any one of normal pressure, increased pressure and reduced pressure. The reaction may be in the air, or in an inactive atmosphere. From the viewpoint of productivity, preferred is the atmosphere of the air having a pressure of 1 atm. About the reaction temperature, the reductive reaction rate becomes larger as the reaction temperature becomes higher. Thus, from the viewpoint of productivity, a high temperature is desirable. However, if the temperature is higher than 100°C , the yield is lowered by side reaction or the like; thus, the temperature is preferably 100°C or lower. On the other hand, room temperature is desirable since reaction operations are easily conducted. If the temperature is lower than 0°C , water freezes. The temperature is preferably 25°C or higher, and 100°C or lower, more preferably 50°C or higher, and 100°C or lower. The reductive reaction time depends on the kind of the ketone compound, the reaction temperature and others; however, the reductive reaction ends completely in a time from about 15 hours to 96 hours.

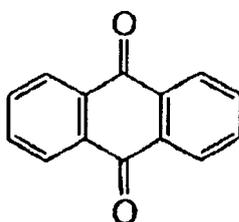
[0049] According to the dimerization reaction of a ketone including an additional active group, a diketone can be produced also in the atmospheric air, which contains oxygen gas. In the atmospheric air, however, a byproduct wherein the active group is oxidized is produced. It is therefore preferred to use an inert gas atmosphere in order to synthesize a diketone compound selectively. The inert gas atmosphere is suitably a nitrogen gas atmosphere from the viewpoint of economy.

[0050] Preferably, a monocrystal C12A7 electride or polycrystal electride is pulverized into powder having an average particle diameter of about 10 μm in a mortar to prepare reductant. The powder is added to a ketone compound, and the components are stirred and mixed in a solvent under conditions described above. Next, in post-treatment, a product is extracted from the reaction solution. The method for the extraction may be a known method adopted as a method for extraction from a reaction solution.

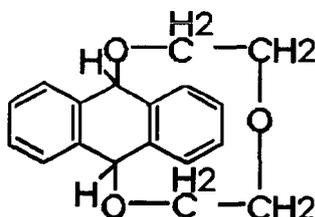
[0051] Specifically, for example, hydrochloric acid is added to the reaction solution, and then, for example, ethyl acetate is added thereto so as to extract the product. This extracting process is repeated about 3 times, and then the product is washed with sodium bicarbonate solution and sodium chloride solution. Thereto is added magnesium sulfate to adsorb water, thereby removing water. Next, magnesium sulfate is filtrated off, and the solvent is distilled off. The resultant is purified by column chromatography (silica gel). The finally produced compound can be separated by the chemical pre-treatment and the column chromatography. The identification of the compound and the rate of the conversion from the raw material can be obtained based on the H^1 nuclear magnetic resonance spectrum.

[0052] The conversion rate of the dimerization reaction of the ketone depends on the kind of the solvent, and the kind of the gas of the reaction atmosphere, and ranges from about 40 to 60%. Whether or not a byproduct is produced, and the chemical structure thereof also depend on the kind of the solvent, and the kind of the gas of the reaction atmosphere. For example, in the reaction of dimerizing anthrone to produce dianthrone, only dianthrone is produced without producing any byproduct when the reaction is conducted in a dry nitrogen atmosphere, using cyanomethane as a solvent. However, when the reaction is conducted in the air, anthraquinone, which is obtained by oxidizing anthrone and is represented by formula [9] illustrated below, is produced with a conversion rate of about 30%. When dioxane is used as the solvent, a byproduct wherein anthrone and dioxane are bonded to each other, which is represented by formula [10] illustrated below, is produced with a conversion rate of about 20%.

[Chemical formula 9]



[Chemical formula 10]



[0053] The invention will be described in more detail by way of the following examples:

(Preparation of a C12A7 electride)

[0054] Prepared was a C12A7 electride having an electron concentration of about $2 \times 10^{21} \text{ cm}^{-3}$ was prepared. This C12A7 electride was produced by the following method: From a C12A7 monocrystal ingot produced by the Czochralski method, a plate, 10 mm \times 10 mm \times 3 mm, was cut out, and then the plate together with metallic Ti was put into a quartz

EP 2 067 761 B1

tube so as to seal the tube in a vacuum. The quartz tube is put into an electric furnace, kept at 1100°C for 24 hours, and then cooled with the air. The electron concentration of the resultant C12A7 electride was obtained by converting the light reflection spectrum of the electride to an optical absorption spectrum and then measuring the intensity of the 2.8-eV absorption band thereof. This monocrystal C12A7 electride was pulverized in a mortar to yield powder having an average particle diameter of about 10 μm .

<Production of Diols or Polydiols>

[Examples 1 to 14]

[0055]

[Table 1]

Example No.	Carbonyl compound *①	C12A7 electricle amount mg (electron concentration:cm ³)	Solvent (volume: ml)	Reactiontime (h)	Reaction temperature (°C)	Conversion rate (%)
1	Benzaldehyde	100(2×10 ²¹)	Water (2)	15	25	More than 95
2	ditto	50(2×10 ²¹)	Water (1)	15	25	More than 95
3	ditto	200(2×10 ²¹)	*② (4)	24	90	More than 95
4	4-Methylbenzaldehyde	131(2×10 ²¹)	Water (4)	19	25	More than 95
5	4-Ethylbenzaldehyde	121(2×10 ²¹)	Water (4)	19	25	More than 95
6	ditto	30(2×10 ²¹)	Water (1)	30	25	More than 95
7	4-t-Butylbenzaldehyde	98(2×10 ²¹)	Water (4)	16	100	More than 95
8	4-Chlorobenzaldehyde	117(2×10 ²¹)	Water (4)	22	100	More than 95
9	4-Methoxybenzaldehyde	120(2×10 ²¹)	Water (2)	72	100	More than 95
10	ditto	120(2×10 ²¹)	Water (4)	20	100	50
11	2-Nitrobenzaldehyde	55(2×10 ²¹)	Water (2)	21	80	73
12	3-Nitrobenzaldehyde	55(2×10 ²¹)	Water (2)	22	80	93
13	4-Hydroxybenzaldehyde	66(2×10 ²¹)	Water (2)	27	25	16
14	4-Cyanobenzaldehyde	62(2×10 ²¹)	Water (2)	22	25	60
15	Benzaldehyde	55(2×10 ¹⁸)	Water (40)	96	25	More than 95

*① 10 mg in Examples 1 to 14, and 26 mg in Example 15
 *② Water: ethanol = 1:4

EP 2 067 761 B1

[0056] Into an eggplant type flask 10 mL in volume were put 10 mg of each carbonyl compound described in Table 1, and further put the C12A7 electride and each solvent in respective amounts shown in Table 1. In the state that the inside thereof was open to the atmosphere, the active components were caused to react with each other at each reaction temperature shown in Table 1 for each reaction time shown therein while the solution was stirred. In this way, a reaction solution was prepared.

[0057] Next, the reaction solution was transferred to an eggplant type flask 50 mL in volume, and hydrochloric acid (1 N, 7 mL) was added thereto. Thereafter, thereto was added ethyl acetate (20 mL) and then the product was extracted. This extracting process was repeated 3 times, and then the product was washed with sodium bicarbonate solution and sodium chloride solution. Thereto was added magnesium sulfate to dry the solution. Thereafter, magnesium sulfate was filtrated off, and the solvent was distilled off. The resultant was purified by column chromatography (silica gel) to yield a diol compound having a purity of more than 98%. The identification of the compound was attained through the H^1 nuclear magnetic resonance spectrum thereof. The product of each of Examples is shown in Table 2. The conversion rate thereof (decrease rate of the carbonyl compound as the starting raw material) is as shown in Table 1.

[Table 2]

Example No.	Produced compound
1	1,2-Diphenyl-1,2-ethandiol
2	1,2-Diphenyl-1,2-ethandiol
3	1,2-Diphenyl-1,2-ethandiol
4	1,2-Bis(4-methylphenyl)-1,2-ethandiol
5	1,2-Bis(4-ethylphenyl)-1,2-ethandiol
6	1,2-Bis(4-ethylphenyl)-1,2-ethandiol
7	1,2-Bis(4-t-butylphenyl)-1,2-ethandiol
8	1,2-Bis(4-chlorophenyl)-1,2-ethandiol
9	1,2-Bis(4-methoxyphenyl)-1,2-ethandiol
10	1,2-Bis(4-methoxyphenyl)-1,2-ethandiol
11	1,2-Bis(2-nitrophenyl)-1,2-ethandiol
12	1,2-Bis(2-nitrophenyl)-1,2-ethandiol
13	1,2-Bis(4-hydroxyphenyl)-1,2-ethandiol
14	1,2-Bis(4-cyanophenyl)-1,2-ethandiol
15	1,2-Diphenyl-1,2-ethandiol

[Example 15]

[0058] A C12A7 electride having an electron concentration of $1 \times 10^{19} \text{ cm}^{-3}$ was produced by the following method: C12A7 powder was put in a carbon crucible with a cover. The powder was heated to 1600°C in the atmosphere so as to be melted. The melt was cooled at a lowering rate of about 400°C /hour to yield polycrystal C12A7. The electron concentration was obtained based on the electron spin resonance spectrum. This polycrystal C12A7 electride was pulverized in a mortar to yield powder having an average particle diameter of about 10 μm .

[0059] In the same way as in Example 1 except that this electride was used, a reaction was conducted under conditions shown in Table 1. However, the amount of benzaldehyde was set to 25 mg. The product was 1,2-diphenyl-1,2-ethandiol, and the conversion rate was more than 95%. This result demonstrated that a reductive coupling reaction of a carbonyl compound occurred even when a C12A7 electride having a small electron concentration is used.

[Comparative Example 1]

[0060] Reaction was conducted under the same conditions as in Example 1 shown in Table 1 except that C12A7 powder having a stoichiometric composition and containing no electrons was used instead of the C12A7 electride. After the reaction, only benzaldehyde was detected, and no reductive coupling reaction was caused.

EP 2 067 761 B1

<Production of Secondary Alcohols or Diketone Compounds>

[Example 16]

5 (Synthesis of a secondary alcohol)

[0061] Into an eggplant type flask 10 mL in volume were put 10 mg of a ketone compound having R and R¹ groups of No. 1 as a raw material (compound 1) shown in Table 3, 196 mg of a C12A7 electrider, and 5 mL of a solvent (water: dioxane = 1:4). In the state that the flask was open to the atmosphere, the active components were caused to react at a reaction temperature shown in Table 3 for a reaction time shown therein while the solution was stirred. Thus, a reaction solution was prepared.

[Table 3]

	Raw material (compound 1)		Electrider (mg)	Solvent	Reaction time	Reaction temperature
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}^1 \end{array}$					
	R	R ¹				
1	Ph-p-CN(p-cyanophenyl)	CH ₃ (methyl)	196	H ₂ O/ dioxane	9 hours	100°C
2	Ph-p-OMe(p-methoxyphenyl)	Ph-p-OMe(p-methoxyphenyl)	229	H ₂ O/ dioxane	17 hours	100°C
3	Ph(phenyl)	Ph(phenyl)	164	H ₂ O/ dioxane	10 hours	100°C

[Table 4]

	Product (compound 2)		Yield
	$\begin{array}{c} \text{OH} \\ \\ \text{R}-\text{C}-\text{R}^1 \\ \\ \text{H} \end{array}$		
	R	R ¹	
1	Ph-p-CN(p-cyanophenyl)	CH ₃ (methyl)	59%
2	Ph-p-OMe(p-methoxyphenyl)	Ph-p-OMe(p-methoxyphenyl)	3%
3	Ph(phenyl)	Ph(phenyl)	57%

[0062] Next, the reaction solution was transferred to an eggplant type flask 50 mL in volume, and hydrochloric acid (1 N, 7 mL) was added thereto. Thereafter, thereto was added ethyl acetate (20 mL) and then the product was extracted. This extracting process was repeated 3 times, and then the product was washed with sodium bicarbonate solution and sodium chloride solution. Thereto was added magnesium sulfate to adsorb water, thereby removing water. Next, magnesium sulfate was filtrated off, and the solvent was distilled off. The resultant was purified by column chromatography (silica gel) to yield a compound having a purity of more than 98%. The identification of the compound was attained through the H¹ nuclear magnetic resonance spectrum thereof. The product (compound 2) is shown in Table 4. The compound was a secondary alcohol represented by the formula of RR¹HC-OH in Table 4. The yield of the purified secondary alcohol was 59%.

[Example 17]

[0063] Reaction was conducted under the same conditions as in Example 16 except that a ketone compound having R and R¹ groups of No. 2 in Table 3 was used as a raw material (compound 1), and the amount of the electrider and the reaction time were set as shown in Table 3. In this way, a secondary alcohol represented by the formula of RR¹HC-OH in Table 4 was yielded. The yield was 3%.

[Example 18]

5 [0064] Reaction was conducted under the same conditions as in Example 16 except that a ketone compound having R and R¹ groups of No. 3 in Table 3 was used as a raw material (compound 1), and the amount of the electride and the reaction time were set as shown in Table 3. In this way, a secondary alcohol represented by the formula of RR¹HC-OH in Table 4 was yielded. The yield was 57%.

[Example 19]

10 (Synthesis of dianthrone)

[0065] Into a mixed solvent of water and cyanomethane (1:4) were put 10 mg of anthrone, and 164 mg of a C12A7 electride, and then the solution was put into an eggplant type flask 10 mL in volume. In the atmosphere of nitrogen gas, the active components were caused to react at 100°C for 12 hours while the solution was stirred.

15 [0066] Next, the reaction solution was transferred to an eggplant type flask 50 mL in volume, and hydrochloric acid (1 N, 7 mL) was added thereto. Thereafter, thereto was added ethyl acetate (20 mL) and then the product was extracted. This extracting process was repeated 3 times, and then the product was washed with sodium bicarbonate solution and sodium chloride solution. Thereto was added magnesium sulfate to adsorb water, thereby removing water. Next, magnesium sulfate was filtrated off, and the solvent was distilled off. The resultant was purified by column chromatography
20 (silica gel) to yield a compound having a purity of more than 98%. The identification of the compound was attained through the H¹ nuclear magnetic resonance spectrum thereof. The compound was dianthrone. The yield of the product was 45%, which was calculated from the weight of the product.

[Example 20]

25 (Synthesis of dichalcone)

[0067] Into a mixed solvent of water and THF (1:4) were put 100 mg of chalcone, and 1200 mg of a C12A7 electride, and then the solution was put into an eggplant type flask 10 mL in volume. In the atmosphere of nitrogen gas, the active
30 components were caused to react at 25°C for 18 hours while the solution was stirred. In this way, a reaction solution was prepared.

[0068] Next, the reaction solution was transferred to an eggplant type flask 50 mL in volume, and hydrochloric acid (1 N, 7 mL) was added thereto. Thereafter, thereto was added ethyl acetate (20 mL) and then the product was extracted. This extracting process was repeated 3 times, and then the product was washed with sodium bicarbonate solution and
35 sodium chloride solution. Thereto was added magnesium sulfate to adsorb water, thereby removing water. Next, magnesium sulfate was filtrated off, and the solvent was distilled off. The resultant was purified by column chromatography (silica gel) to yield compounds. The identification of the compounds was attained through the H¹ nuclear magnetic resonance spectra thereof. The compounds were a mixture of dichalcones represented by the formula of compound 6 and compound 7. The yield of the compound 6 was 5% and that of the compound 7 was 23%, which were each calculated
40 from the weight of the product.

[Comparative Example 2]

45 [0069] Reaction was conducted under the same conditions as in Example 16 except that C12A7 powder having a stoichiometric composition and containing no electrons was used instead of the C12A7 electride. After the reaction, only the ketone compound was detected, and no reductive reaction was caused.

Industrial Applicability

50 [0070] The invention provides a process for synthesizing a secondary alcohol or diketone, or a diol or polydiol, as defined in the claims, which is used as an intermediate compound for medicine, or the like, with a high yield in a short time. The reaction therefore is a reaction that does not need any catalyst, such as a heavy metal, and is conducted in an aqueous solvent or a mixed solvent of water and an organic solvent. Thus, provided is a safe and environment-
55 friendly synthesizing process for which no harmful material is necessary. Provided is also an inexpensive synthesizing process since the reaction can be attained at room temperature in the atmosphere.

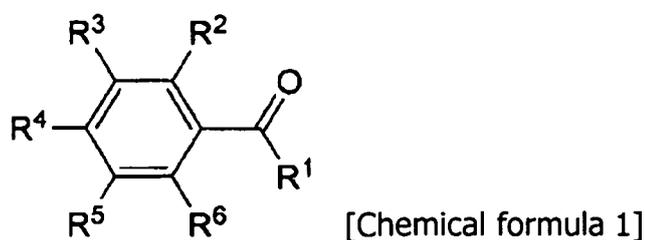
Claims

1. A process for producing a diol or polydiol by reductive coupling reaction of a carbonyl compound in a reaction solution, comprising:

forming the reaction solution by mixing the carbonyl compound and a $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride containing electrons in a number of 10^{19} cm^{-3} or more and $2.3 \times 10^{21}\text{ cm}^{-3}$ or less in its cages in water, an organic solvent, or a mixed solvent of water and an organic solvent, wherein about the use amount of the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride relative to the carbonyl compound ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3/\text{the carbonyl compound}$), the ratio by weight of the former to the latter is from 2 to 20, and extracting a product from the reaction solution.

2. The process for producing a diol or polydiol according to claim 1, wherein the carbonyl compound is a compound wherein at least one out of two substituents bonded to a carbonyl group is an aryl group.

3. The process for producing a diol or polydiol according to claim 1, wherein the carbonyl compound is represented by the following general formula:

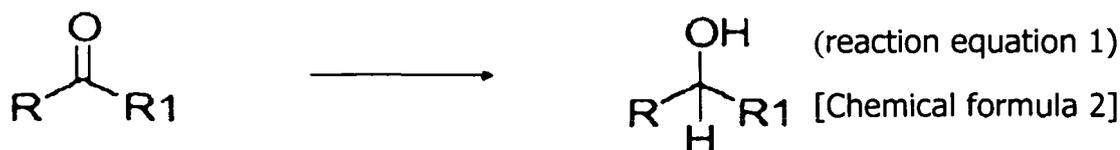


wherein R^1 is a functional group selected from a hydrogen atom, an alkyl group and an aryl group, R^2 , R^3 , R^4 , R^5 and R^6 are each a functional group, bonded to the aryl group, selected from a hydrogen atom, a chloro radical, a bromo radical, an iodo radical, an alkyl group, an aryl group, a carbonyl group, an allyl group, a vinyl group, an amino group, a hydroxy group, an alkoxy group, a nitro group, a cyano group, and an imino group, and R^1 and the aryl group may be bonded to each other to form a ring structure.

4. The process for producing a diol or polydiol according to claim 1, wherein a reaction atmosphere for the reductive coupling is the inside of air.

5. A process for producing a secondary alcohol by reductive reaction of a ketone compound in a reaction solution, comprising:

forming the reaction solution by mixing the ketone compound represented by compound 1 in the following reaction equation 1 and a $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride containing electrons in a number of 10^{19} cm^{-3} or more and $2.3 \times 10^{21}\text{ cm}^{-3}$ or less in its cages in water, an organic solvent, or a mixed solvent of water and an organic solvent, wherein about the use amount of the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride relative to the ketone compound ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3/\text{the ketone compound}$), the ratio by weight of the former to the latter is from 2 to 20, and extracting a product from the reaction solution, thereby synthesizing the secondary alcohol which is a secondary alcohol represented by compound 2 in the reaction equation 1:

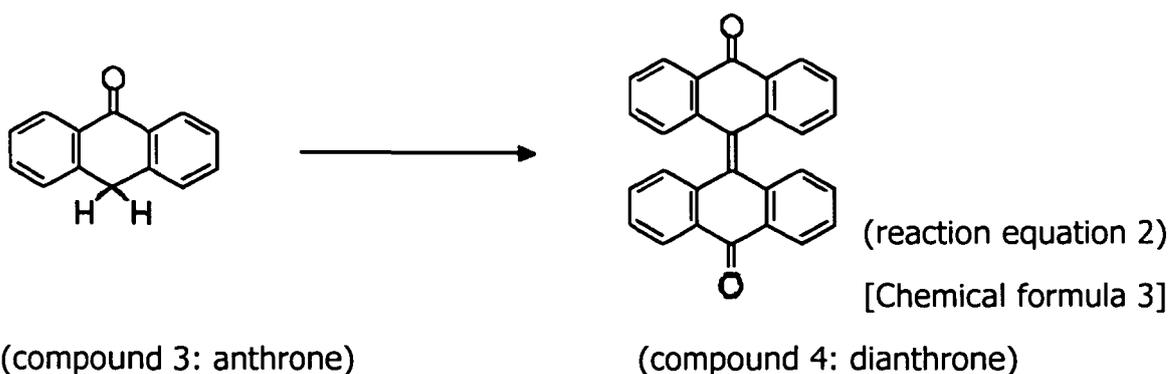


(compound 1: ketone)

(compound 2: secondary alcohol)

wherein R and R¹ are each a functional group selected from an aryl group and an alkyl group, and at least one of R and R¹ contains an aryl group.

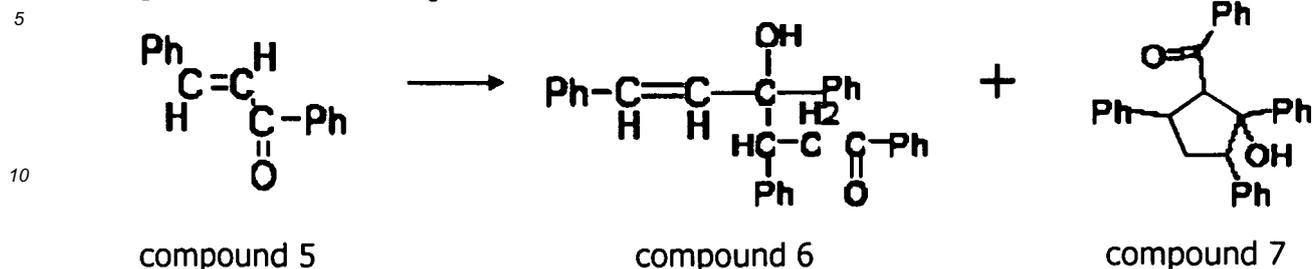
6. The process for producing a secondary alcohol according to claim 5, wherein R and R¹ are each at least one selected from a methyl group, a phenyl group, a phenylcyano group, or a phenylmethoxy group, except that R and R¹ are simultaneously methyl groups.
7. The process for producing a secondary alcohol according to claim 5, wherein the organic solvent, or the organic solvent of the mixed solvent is dioxane.
8. The process for producing a secondary alcohol according to claim 5, wherein an atmosphere for the reaction is the inside of the air.
9. A process for producing a dianthrone by dimerization of an arylketone compound in a reaction solution, comprising; forming the reaction solution by mixing the arylketone compound (anthrone) represented by compound 3 in the following reaction equation 2 and a 12CaO·7Al₂O₃ electrone containing electrons in a number of 10¹⁹ cm⁻³ or more and 2.3 × 10²¹ cm⁻³ or less in its cages in a mixed solvent of water and an organic solvent, wherein about the use amount of the 12CaO·7Al₂O₃ electrone relative to the ketone compound (12CaO·7Al₂O₃/the ketone compound), the ratio by weight of the former to the latter is from 2 to 20, and extracting a product from the reaction solution, thereby synthesizing the dianthrone which is a dianthrone represented by compound 4 in the reaction equation 2:



10. The process for producing a dianthrone according to claim 9, wherein the organic solvent is selected from CH₃CN, Et-OH, t-Bu-OH, or dioxane.
11. The process for producing a dianthrone according to claim 9, wherein an atmosphere for the reaction is the inside of an inert gas.
12. A process for producing a dichalcone mixture by dimerizing a ketone compound in a reaction solution, comprising; forming the reaction solution by mixing the ketone compound (chalcone) represented by compound 5 in the following reaction equation 3, which contains a carbon double bond, and a 12CaO·7Al₂O₃ electrone containing electrons in a number of 10¹⁹ cm⁻³ or more and 2.3 × 10²¹ cm⁻³ or less in its cages in a mixed solvent of water and an organic solvent, wherein about the use amount of the 12CaO·7Al₂O₃ electrone relative to the ketone compound (12CaO·7Al₂O₃/the ketone compound), the ratio by weight of the former to the latter is from 2 to 20, and extracting a product from the reaction solution, thereby synthesizing dichalcones represented by compound 6 and compound 7 in the reaction equation 3:

(reaction equation 3)

[Chemical formula 4]



13. The process for producing a dichalcone according to claim 12, wherein the organic solvent is tetrahydrofuran (THF).

Patentansprüche

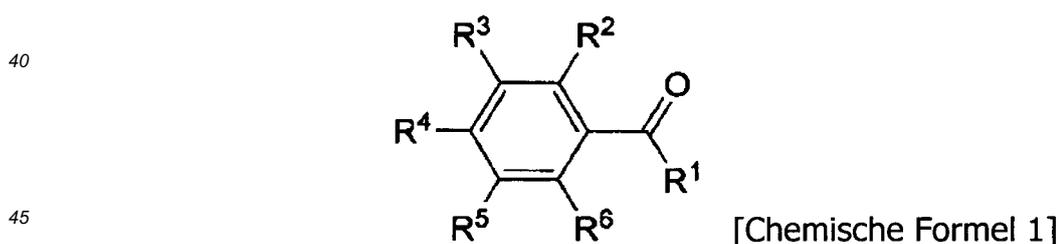
20 1. Verfahren zum Herstellen eines Diols oder Polydiols durch reduktive Kupplungsreaktion einer Carbonylverbindung in einer Reaktionslösung, umfassend:

25 Bilden der Reaktionslösung durch Mischen der Carbonylverbindung und einem $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrid, enthaltend Elektronen in einer Anzahl von 10^{19} cm^{-3} oder mehr und $2,3 \times 10^{21}\text{ cm}^{-3}$ oder weniger in dessen Käfigen, in Wasser, einem organischen Lösungsmittel, oder einem gemischten Lösungsmittel von Wasser und organischem Lösungsmittel, wobei etwa die Verwendungsmenge des $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrid in Bezug auf die Carbonylverbindung ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3/\text{die Carbonylverbindung}$), das Gewichtsverhältnis des Ersteren zu dem Letzteren von 2 bis 20 beträgt, und

30 Extrahieren eines Produkts aus der Reaktionslösung.

2. Verfahren zum Herstellen eines Diols oder Polydiols nach Anspruch 1, wobei die Carbonylverbindung eine Verbindung ist, worin mindestens einer von zwei Substituenten, die mit einer Carbonylgruppe verbunden sind, eine Arylgruppe ist.

35 3. Verfahren zum Herstellen eines Diols oder Polydiols nach Anspruch 1, wobei die Carbonylverbindung dargestellt ist durch die folgende allgemeine Formel:



wobei R^1 eine funktionelle Gruppe ist, ausgewählt aus einem Wasserstoffatom, einer Alkylgruppe und einer Arylgruppe, R^2 , R^3 , R^4 , R^5 und R^6 jeweils eine funktionelle Gruppe sind, gebunden an die Arylgruppe, ausgewählt aus einem Wasserstoffatom, einem Chlorradikal, einem Bromradikal, einem Iodradikal, einer Alkylgruppe, einer Arylgruppe, einer Carbonylgruppe, einer Allylgruppe, einer Vinylgruppe, einer Aminogruppe, einer Hydroxygruppe, einer Alkoxygruppe, einer Nitrogruppe, einer Cyanogruppe, und einer Iminogruppe, und R^1 und die Arylgruppe können miteinander gebunden sein, um eine Ringstruktur auszubilden.

55 4. Verfahren zum Herstellen eines Diols oder Polydiols nach Anspruch 1, wobei eine Reaktionsatmosphäre für die reduktive Kupplung innerhalb von Luft ist.

5. Verfahren zum Herstellen eines sekundären Alkohols durch reduktive Reaktion einer Ketonverbindung in einer

Reaktionslösung, umfassend:

Bilden der Reaktionslösung durch Mischen der Ketonverbindung, dargestellt durch Verbindung 1 in der folgenden Reaktionsgleichung 1, und einem $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrizität, enthaltend Elektronen in einer Anzahl von 10^{19} cm^{-3} oder

mehr und $2,3 \times 10^{21}$ cm^{-3} oder weniger in dessen Käfigen, in Wasser, einem organischen Lösungsmittel, oder einem gemischten Lösungsmittel von Wasser und organischem Lösungsmittel, wobei etwa die Verwendungsmenge des $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrizität in Bezug auf die Ketonverbindung ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ /die Ketonverbindung), das Gewichtsverhältnis des Ersteren zu dem Letzteren von 2 bis 20 beträgt, und

Extrahieren eines Produkts aus der Reaktionslösung;
dadurch Synthetisieren des sekundären Alkohols, der ein sekundärer Alkohol ist, dargestellt durch Verbindung 2 in der Reaktionsgleichung 1:



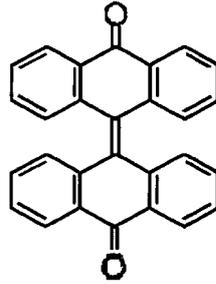
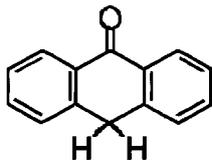
(Verbindung 1: Keton)

(Verbindung 2: sekundärer Alkohol)

wobei R und R^1 jeweils eine funktionelle Gruppe sind, ausgewählt aus einer Arylgruppe und einer Alkylgruppe, und mindestens einer von R und R^1 enthält eine Arylgruppe.

6. Verfahren zum Herstellen eines sekundären Alkohols nach Anspruch 5, wobei R und R^1 jeweils mindestens eines sind, ausgewählt aus einer Methylgruppe, einer Phenylgruppe, einer Phenylcyanogruppe oder einer Phenylmethoxygruppe, außer das R und R^1 gleichzeitig Methylgruppen sind.
7. Verfahren zum Herstellen eines sekundären Alkohols nach Anspruch 5, wobei das organische Lösungsmittel oder das organische Lösungsmittel des gemischten Lösungsmittels Dioxan ist.
8. Verfahren zum Herstellen eines sekundären Alkohols nach Anspruch 5, wobei eine Reaktionsatmosphäre für die reduktive Kupplung innerhalb von Luft ist.
9. Verfahren zum Herstellen eines Dianthrone durch Dimerisierung einer Arylketonverbindung in einer Reaktionslösung, umfassend;
Bilden der Reaktionslösung durch Mischen der Arylketonverbindung (Anthrone), dargestellt durch Verbindung 3 in der folgenden Reaktionsgleichung 2, und einem $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrizität, enthaltend Elektronen in einer Anzahl von 10^{19} cm^{-3} oder mehr und $2,3 \times 10^{21}$ cm^{-3} oder weniger in dessen Käfigen, in einem gemischten Lösungsmittel von Wasser und organischem Lösungsmittel, wobei etwa die Verwendungsmenge des $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrizität in Bezug auf die Ketonverbindung ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ /die Ketonverbindung), das Gewichtsverhältnis des Ersteren zu dem Letzteren von 2 bis 20 beträgt, und
Extrahieren eines Produkts aus der Reaktionslösung
dadurch Synthetisieren des Dianthrone, welches ein Dianthrone ist, dargestellt durch Verbindung 4 in der Reaktionsgleichung 2:

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(Reaktionsgleichung 2)

[Chemische Formel 3]

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(Verbindung 3: Anthron)

(Verbindung 4: Dianthron)

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10. Verfahren zum Herstellen eines Dianthrons nach Anspruch 9, wobei das organische Lösungsmittel ausgewählt ist aus CH_3CN , Et-OH, t-Bu-OH, oder Dioxan.

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11. Verfahren zum Herstellen eines Dianthrons nach Anspruch 9, wobei eine Reaktionsatmosphäre innerhalb eines Inertgases ist.

12. Verfahren zum Herstellen eines Dichalcongemeschtes durch Dimerisieren einer Ketonverbindung in einer reaktiven Lösung, umfassend;

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Bilden der Reaktionslösung durch Mischen der Ketonverbindung (Chalcon) dargestellt durch Verbindung 5 in der folgenden Reaktionsgleichung 3, welche eine Kohlenstoffdoppelbindung enthält, und einem $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrizid, enthaltend Elektronen in einer Anzahl von 10^{19} cm^{-3} oder mehr und $2,3 \times 10^{21}\text{ cm}^{-3}$ oder weniger in dessen Käfigen, in einem gemischten Lösungsmittel von Wasser und organischem Lösungsmittel, wobei etwa die Verwendungsmenge des $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Elektrizid in Bezug auf die Ketonverbindung ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3/\text{die Ketonverbindung}$), das Gewichtsverhältnis des Ersteren zu dem Letzteren von 2 bis 20 beträgt, und

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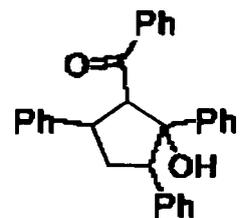
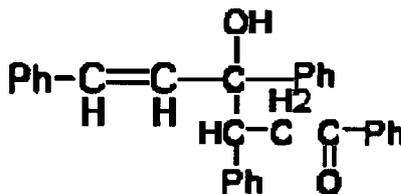
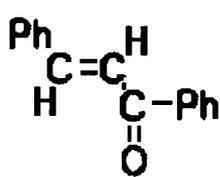
Extrahieren eines Produkts aus der Reaktionslösung, dadurch Synthetisieren von Dichalconen, dargestellt durch Verbindung 6 und Verbindung 7 in der Reaktionsgleichung 3:

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(Reaktionsgleichung 3)

[Chemische Formel 4]

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Verbindung 5

Verbindung 6

Verbindung 7

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13. Verfahren zum Herstellen eines Dichalcon nach Anspruch 12, wobei das organische Lösungsmittel Tetrahydrofuran (THF) ist.

Revendications

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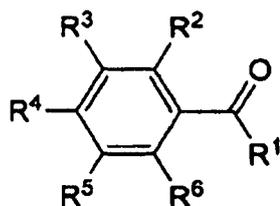
1. Procédé de production d'un diol ou d'un polydiol par une réaction de couplage réducteur d'un composé carbonyle dans une solution réactionnelle, comprenant :

la formation de la solution réactionnelle en mélangeant le composé carbonyle et un électrolyte $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$

EP 2 067 761 B1

contenant des électrons dans un nombre de 10^{19} cm^{-3} ou plus et $2,3 \times 10^{21} \text{ cm}^{-3}$ ou moins dans ses cages dans l'eau, un solvant organique, ou un solvant mixte d'eau et d'un solvant organique, dans lequel, quant à la quantité d'utilisation de l'électrure $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ par rapport au composé carbonyle ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ /le composé carbonyle), le rapport en poids du premier sur le dernier est de 2 à 20, et l'extraction d'un produit de la solution réactionnelle.

2. Procédé de production d'un diol ou d'un polydiol selon la revendication 1, dans lequel le composé carbonyle est un composé dans lequel au moins un parmi deux substituants liés à un groupe carbonyle est un groupe aryle.
3. Procédé de production d'un diol ou d'un polydiol selon la revendication 1, dans lequel le composé carbonyle est représenté par la formule générale suivante :

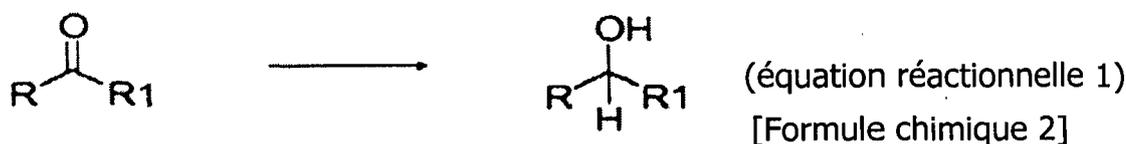


[Formule chimique 1]

dans laquelle R¹ est un groupe fonctionnel choisi parmi un atome d'hydrogène, un groupe alkyle et un groupe aryle, R², R³, R⁴, R⁵ et R⁶ sont chacun un groupe fonctionnel, lié au groupe aryle, choisi parmi un atome d'hydrogène, un radical chloro, un radical bromo, un radical iodo, un groupe alkyle, un groupe aryle, un groupe carbonyle, un groupe allyle, un groupe vinyle, un groupe amino, un groupe hydroxy, un groupe alcoxy, un groupe nitro, un groupe cyano, et un groupe imino, et R¹ et le groupe aryle peuvent être liés l'un à l'autre pour former une structure cyclique.

4. Procédé de production d'un diol ou d'un polydiol selon la revendication 1, dans lequel une atmosphère de réaction pour le couplage réducteur est l'intérieur de l'air.
5. Procédé de production d'un alcool secondaire par une réaction réductrice d'un composé cétone dans une solution réactionnelle, comprenant :

la formation de la solution réactionnelle en mélangeant le composé cétone représenté par le composé 1 dans l'équation réactionnelle 1 suivante et un électrure $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ contenant des électrons dans un nombre de 10^{19} cm^{-3} ou plus et $2,3 \times 10^{21} \text{ cm}^{-3}$ ou moins dans ses cages dans l'eau, un solvant organique, ou un solvant mixte d'eau et d'un solvant organique, dans lequel, quant à la quantité d'utilisation de l'électrure $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ par rapport au composé cétone ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ /le composé cétone), le rapport en poids du premier sur le dernier est de 2 à 20, et l'extraction d'un produit de la solution réactionnelle, synthétisant ainsi l'alcool secondaire qui est un alcool secondaire représenté par le composé 2 dans l'équation réactionnelle 1 :



(composé 1 : cétone)

(composé 2 : alcool secondaire)

dans lesquelles R et R¹ sont chacun un groupe fonctionnel choisi parmi un groupe aryle et un groupe alkyle, et au moins un de R et R¹ contient un groupe aryle.

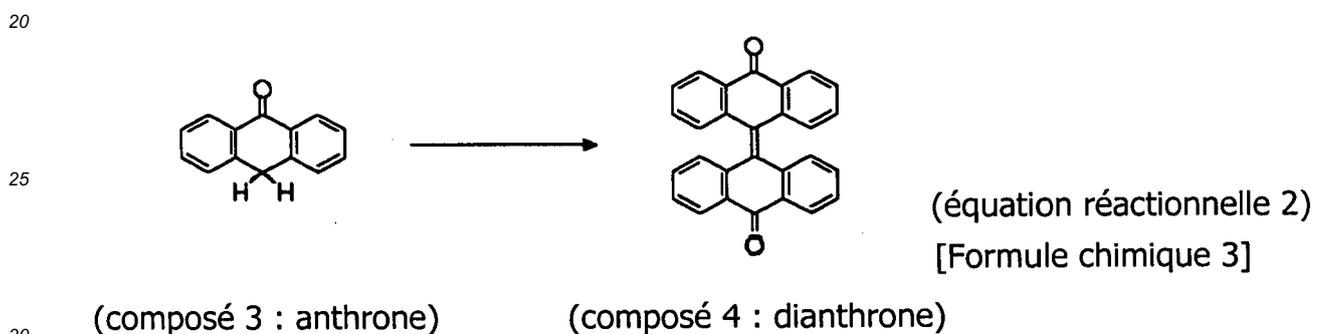
6. Procédé de production d'un alcool secondaire selon la revendication 5, dans lequel R et R¹ sont chacun au moins un choisi parmi un groupe méthyle, un groupe phényle, un groupe phénylcyano, ou un groupe phénylméthoxy, à cette exception que R et R¹ soient simultanément des groupes méthyle.

7. Procédé de production d'un alcool secondaire selon la revendication 5, dans lequel le solvant organique, ou le solvant organique du solvant mixte est le dioxane.

5 8. Procédé de production d'un alcool secondaire selon la revendication 5, dans lequel une atmosphère pour la réaction est l'intérieur de l'air.

9. Procédé de production d'une dianthrone par dimérisation d'un composé arylcétone dans une solution réactionnelle, comprenant :

10 la formation de la solution réactionnelle en mélangeant le composé arylcétone (anthrone) représenté par le composé 3 dans l'équation réactionnelle 2 suivante et un électrode $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ contenant des électrons dans un nombre de 10^{19} cm^{-3} ou plus et $2,3 \times 10^{21}\text{ cm}^{-3}$ ou moins dans ses cages dans un solvant mixte d'eau et d'un solvant organique, dans lequel, quant à la quantité d'utilisation de l'électrode $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ par rapport au composé cétone ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ /le composé cétone), le rapport en poids du premier sur le dernier est de 2 à 20, et l'extraction d'un produit de la solution réactionnelle, synthétisant ainsi la dianthrone qui est une dianthrone représentée par le composé 4 dans l'équation réactionnelle 2 :

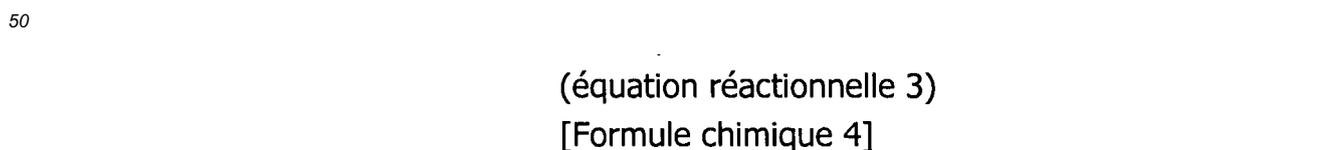


10. Procédé de production d'une dianthrone selon la revendication 9, dans lequel le solvant organique est choisi parmi CH_3CN , Et-OH, t-Bu-OH, ou le dioxane.

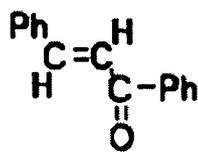
35 11. Procédé de production d'une dianthrone selon la revendication 9, dans lequel une atmosphère pour la réaction est l'intérieur d'un gaz inerte.

12. Procédé de production d'un mélange de dichalcones par dimérisation d'un composé cétone dans une solution réactionnelle, comprenant :

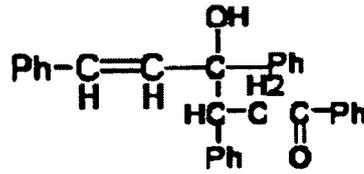
40 la formation de la solution réactionnelle en mélangeant le composé cétone (chalcone) représenté par le composé 5 dans l'équation réactionnelle 3 suivante, qui contient une liaison carbone double, et un électrode $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ contenant des électrons dans un nombre de 10^{19} cm^{-3} ou plus et $2,3 \times 10^{21}\text{ cm}^{-3}$ ou moins dans ses cages dans un solvant mixte d'eau et d'un solvant organique, dans lequel, quant à la quantité d'utilisation de l'électrode $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ par rapport au composé cétone ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ /le composé cétone), le rapport en poids du premier sur le dernier est de 2 à 20, et l'extraction d'un produit de la solution réactionnelle, synthétisant ainsi des dichalcones représentées par le composé 6 et le composé 7 dans l'équation réactionnelle 3 :



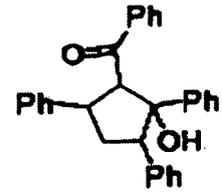
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composé 5



composé 6



composé 7

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13. Procédé de production d'une dichalcone selon la revendication 12, dans lequel le solvant organique est le tétrahydrofurane (THF).

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REFERENCES CITED IN THE DESCRIPTION

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