(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 673 321 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Description Paragraph(s) 13, 28, 29

(48) Corrigendum issued on:
22.04.2015 Bulletin 2015/17

(45) Date of publication and mention
of the grant of the patent:
17.09.2014 Bulletin 2014/38

(21) Application number: **04793476.5**

(22) Date of filing: **13.10.2004**

(51) Int Cl.:
C07C 1/20 $^{(2006.01)}$
C07C 13/15 $^{(2006.01)}$
C07F 17/00 $^{(2006.01)}$
C07C 43/162 $^{(2006.01)}$
C07C 43/192 $^{(2006.01)}$

(86) International application number:
PCT/KR2004/002614

(87) International publication number:
WO 2005/035470 (21.04.2005 Gazette 2005/16)

(54) METHOD OF PREPARING FULVENE COMPOUNDS AND METHOD OF PREPARING ANSA-METALLOCENE COMPOUNDS USING THE COMPOUNDS

VERFAHREN ZUR HERSTELLUNG VON FULVENVERBINDUNGEN UND VERFAHREN ZUR HERSTELLUNG VON ANSA-METALLOCEN-VERBINDUNGEN UNTER ANWENDUNG DER VERBINDUNGEN

PROCEDE DE PREPARATION DE COMPOSES FULVENE ET PROCEDE DE PREPARATION DE COMPOSES ANSA-METALLOCENE AU MOYEN DE CES COMPOSES

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR

(30) Priority: **14.10.2003 KR 2003071444**

(43) Date of publication of application:
28.06.2006 Bulletin 2006/26

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Description

Technical Field

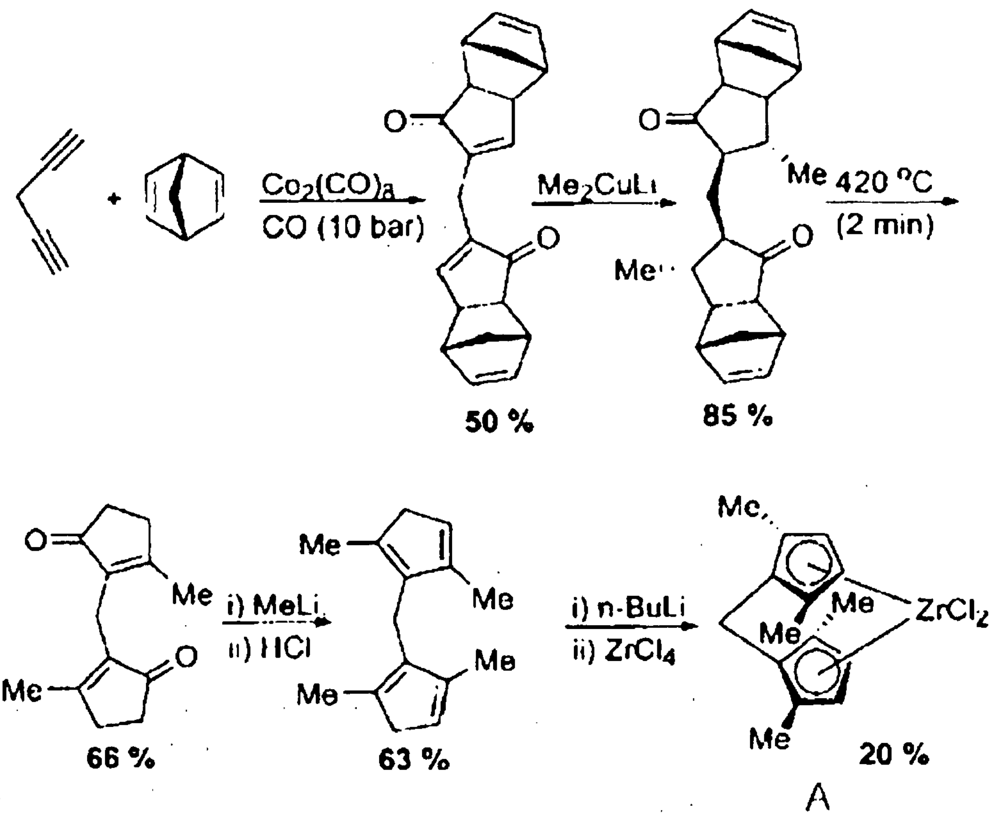
[0001] The present invention relates to a simple method of preparing 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compounds, and a novel intermediate derived from the method. Also, the present invention relates to a method of preparing an ansa-metallocene compound using the fulvene compound and the novel intermediate. Particularly, the present invention relates to a simple, mass-producible method of preparing an ansa- metallocene compound having substituents only at positions adjacent to the bridging point of cyclopentadienyl ligand(s).

Background Art

[0002] The ansa- metallocene compound can be vitally used as an olefin polymerisation catalyst.

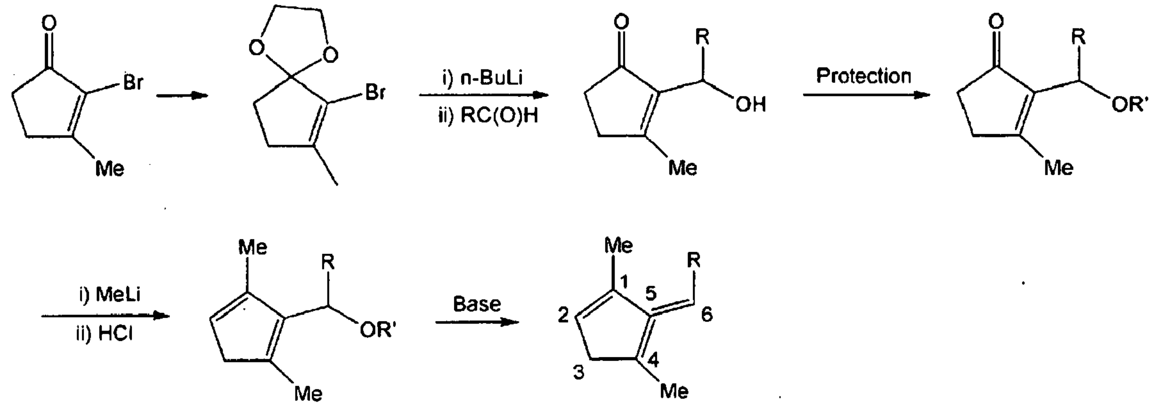
[0003] The ansa- metallocene catalyst having substituents only at positions adjacent to the bridging point was proposed by the present inventor. The present inventor demonstrated that an excellent performance is obtained when a monomer having high steric hindrance, such as a norbornene, is copolymerised with an ethylene, due to low steric hindrance at reaction point, by the ansa-metallocene catalyst. See Korean Patent Application No. 10-98-12658; Organometallics , 2002, 21, 1500-1503 and J. Organomet. Chem., 2002, 660 , 161-166. However, as shown in Reaction Scheme I below, the preparation method is not easy one, and thus has a problem in mass production. Particularly, the synthesis of 1,4-pentadiyne, a starting material of the preparation process of the ansa- metallocene catalyst, is not commercially available. A serial procedure consisting of incorporating a substituent via Pauson-Khand reaction by using the starting material and performing the reverse Diels-Alder reaction is performed at a stringent condition, such as high temperature or high pressure, has many reaction steps, and needs separating-purifying operation by chromatography method, etc. for the intermediates of each reaction steps. Further, the Reaction Scheme has disadvantage that the process use excessive amounts of methyllithium which is dangerous and expensive. Accordingly, the catalyst cannot be easily prepared in commercially significant amounts by Reaction Scheme I below, due to such reasons.

Reaction Scheme I

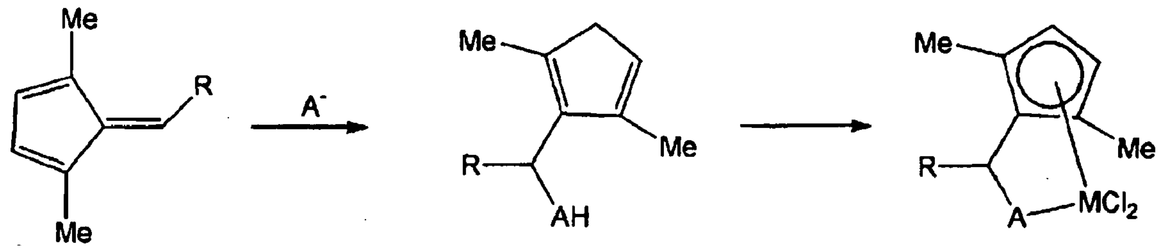


[0004] For the method of more easily preparing the metallocene catalysts having a substituent at positions adjacent to the bridging point, the method of preparing 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compound according to Reaction Scheme II below (Korean Patent Application No. 10-2002-51425) and the method of preparing the metallocene catalyst according to Reaction Scheme III by employing the former method (Korean Patent Application No. 10-2002-51426) have been filed previously.

Reaction Scheme II



Reaction Scheme III



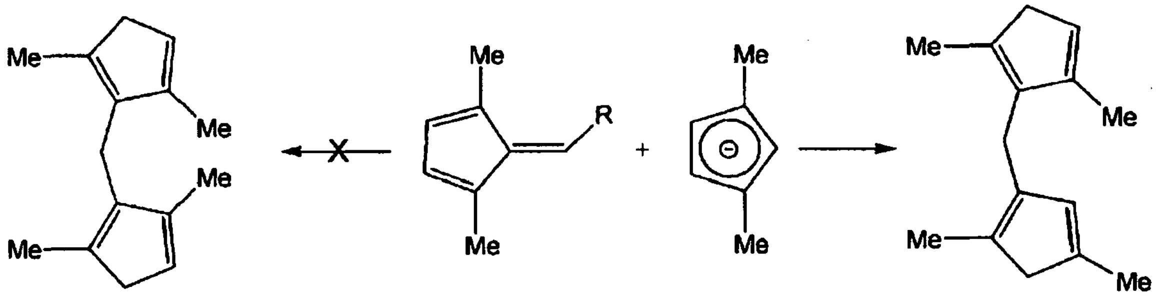
[0005] WON Y C ET AL: "Fulvene having substituents only on 1-, 4-, and 6-positions: a key intermediate for novel ansa-metallocene complexes", JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 677, no. 1-2, 1 July 2003 (2003-07-01), pages 133-139, XP004433255, ISSN: 0022-328X, DOI: DOI:10.1016/S0022-328X(03)00388-7 does not disclose specifically a compound of formula VII (this formula, as well as the other ones cited afterwards are disclosed in the following pages of the description), but refers to a process for producing a compound of formula VIII, inter alia neither even hinting at a compound of formula I, nor obtaining the compound of Formula V by reacting the resulting salt of the lithiation with an electrophile, nor reacting the compound of Formula V with the compound of Formula VI. Furthermore, such known process provides for the addition of methyl lithium to a compound having a carbonyl group.

Disclosure of Invention

Technical Problem

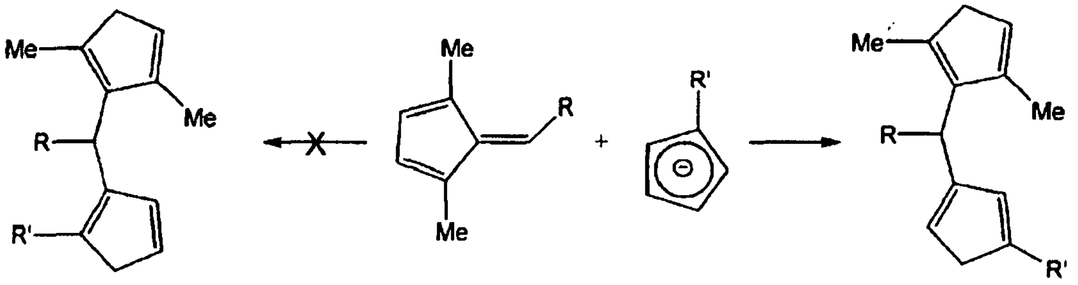
[0006] However, the preparation steps are also too complicated for this case. Particularly, these include protecting-deprotecting steps which are not preferable for mass production such as protection of a ketone to a ketal, organometallic reaction, and then deprotection of the ketal. Further, even though various metallocene catalysts can be prepared by the Reaction Scheme III from the new fulvene prepared by the Reaction Scheme II, the compound A of the Reaction Scheme I cannot be prepared. According to the patent applications, a novel metallocene compound is prepared by preparing a ligand through nucleophilic attack of a cyclopentadienyl, an indenyl, a fluorenyl, an amido, a phosphino anion or their derivatives to a fulvene, and then attaching a metal to the ligand. Reaction of 1,3-dimethylcyclopentadienyl anion is with a 1,4-dimethylfulvene, for the purpose of preparation of the compound A of the Reaction Scheme I, affords a compound having methyl groups at 1- and 4-positions according to the rightward direction in the Reaction Scheme IV below due to the steric hindrance effect, instead of the desired ligand by the reaction of leftward direction of the scheme.

Reaction Scheme IV



[0007] For the sane reason, incorporation of monosubstituted cyclopentadienyl anion into the fulvene shown in Reaction Scheme V below will afford a ligand having a substituent at β-position instead of a ligand having a substituent at α-position.

Reaction Scheme V



[0008] The present invention provides the methods capable of overcoming two problems described above. The present invention provides a method of preparing 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compound in short steps without protecting-deprotecting procedures. Further, the present invention provides a method of easily preparing a metallocene compound having a substituent only at positions adjacent to a bridging point as shown in the Reaction Schemes IV and V.

Technical Solution

[0009] The present invention provides a method of preparing a 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compound, as claimed.

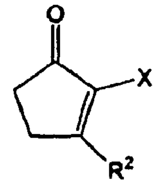
[0010] According to an aspect of the present invention, there is provided an intermediate compound in preparing a metallocene compound having substituents only at positions adjacent to a bridging point, and a method of preparing the same, as claimed.

[0011] According to another aspect of the present invention, there is provided a method of preparing an ansa-metallocene compound in which two cyclopentadienyl ligands are bridged by one carbon and there are substituents only at positions adjacent to the bridging point of a cyclopentadienyl ligand, using the fulvene compound and the novel intermediate, as claimed.

[0012] The present invention will be described in more detail by describing embodiments thereof.

[0013] The present invention provides a method of preparing a 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compound comprising

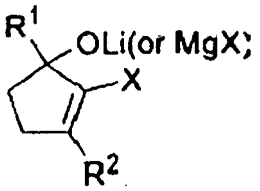
a) reacting Formula I below with a compound of Formula IIa or IIb below to prepare a compound of Formula III below;



(I)

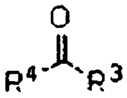
R^1-li (IIa)

R^1-MgX (IIb)

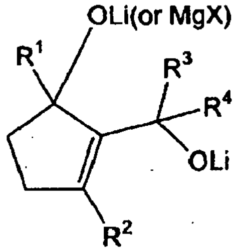


(III)

b) lithiating the compound of the Formula III, and then reacting the resulting lithium salt with an electrophile of Formula IV below to prepare a compound of Formula V below;



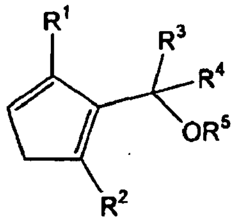
(IV)



(V)

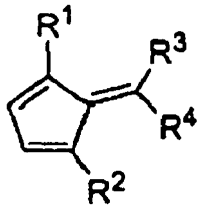
c) reacting the compound of the Formula V with more than one equivalent of a compound of Formula VI below to prepare an ether, and then dehydrating with an acid catalyst to prepare a compound of Fomula VII below; and

R^5-Y (VI)



(VII)

d) adding a base to the compound of the Formula VII to prepare a fulvene compound of Formula VIII



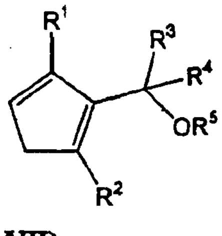
(VIII).

In the Formulae I~VIII,

R^1, R^2, R^3 and R^4 are each independently or simultaneously a hydrogen atom; a C_1-C_{20} alkyle or aryl comprising optionally an oxygen atom; or a C_1-C_{20} alkenyl, alkylaryl or arylalkyl, and
R^1 is not a hydrogen atom, and R^3 and R^4 can be connected together by an alkylidene radical comprising a C_1 -C_{20} alkyl or aryl radical to form a ring;
X is a halogen atom;
R^5 is a C_1-C_{20} alkyl, alkenyl, alkylaryl, or a radical of Group XIV metal substituted with an arylalkyl, an aryl, an alkoxyalkyl or a hydrocarbyl;
Y is a leaving group formed by a nucleophilic substitution reaction.

[0014] It is provided a precursor (Formula VII) of the fulvene compound from which a 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compound (Formula VIII) can be easily obtained by a chemical treatment. The compound of the Formula VII or the compound of the Formula VIII are prepared via the compound of the Formula III.

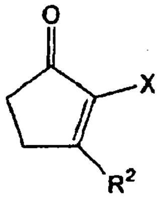
[0015] Thus, the present invention provides a method of preparing the compound of Formula VII below



(VII).

[0016] Specifically, the method of preparing the compound of the Formula VII comprises

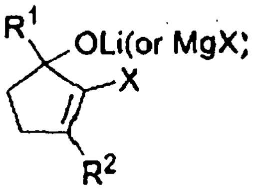
a) reacting Formula I below with a compound of Formula IIa or IIb below to prepare a compound of Fomula III below;



(I)

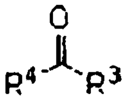
R^1-li (IIa)

R^1-MgX (IIb)



(III)

b) lithiating the compound of the Formula III, and then reacting the resulting lithium salt with an electrophile of Formula IV below to prepare a compound of Formula V below; and



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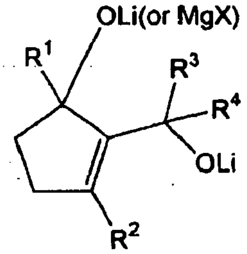
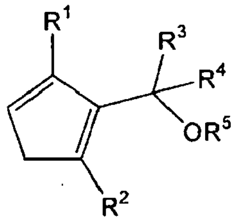


(V)

c) reacting the compound of the Formula V with more than one equivalent of a compound of Formula VI below to prepare an ether, and then dehydrating with an acid catalyst to prepare a compound of Formula VII below

R^5-Y (VI)



(VII).

[0017] In the Formula I~VII,

R^1, R^2, R^3, R^4, R^5, X and Y are the same as defined above.

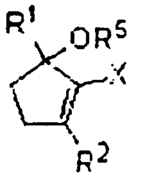
[0018] The 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compound (Formula VIII) can be formed by adding a base to the compound of the Formula VII.

[0019] The specific examples of the compound of the Formula I used in the step a) include 2-bromo-2-cyclopentene-1-one, 2-bromo-3-methyl-2-cyclopentene-1-one, 2-bromo-3-ethyl-2-cyclopentene-1-one, 2-iodo-2-cyclopentene-1-one, 2-iodo-3-methyl-2-cyclopentene-1-one, 2-iodo-3-ethyl-2-cyclopentene-1-one, 2-bromo-3-propyl-2-cyclopentene-1-one, 2-bromo-3-phenyl-2-cyclopentene-1-one, 2-iodo-3-phenyl-2-cyclopentene-1-one, 2-bromo-3-butyl-2-cyclopentene-1-one, 2-bromo-3-tolyl-2-cyclopentene-1-one, 2-bromo-3-ethenyl-2-cyclopentene-1-one, 2-bromo-3-prophenyl-2-cyclopentene-1-one, 2-bromo-3-cumyl-2-cyclopentene-1-one, etc. Of these compounds, 2-bromo-2-cyclopentene-1-one, 2-bromo-3-methyl-2-cyctopentene-1-one and 2-iodo-3-methyl-2-cyclopentene-1-one, etc. are preferable.

[0020] The specific examples of the compound of the Formula IV used as the reactant in the step b) include acetone, formaldehyde, acetaldehyde, benzaldehyde, benzophenone, methylethylketone, butyraldehyde, propionaldehyde, etc. Of these compounds, formaldehyde, acetaldehyde and benzaldehyde, etc. are preferable.

[0021] The examples of the leaving group formed by the nucleophilic substitution reaction in the compound of the Formula VI used as a reactant in the step c) include chlorine, bromine, iodide, methoxymethyl, trifluorosulfonate, and paratoluenesulfonate, etc.

[0022] Further, the present invention provides an intermediate compound of Formula IX in preparing a metallocene compound having a substituent only at positions adjacent to a bridging point, and a method of preparing the same. The compound of the Formula IX can be prepared by reacting the compound of the Formula III below with the compound of the Formula VI below.



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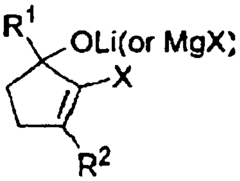


(III)

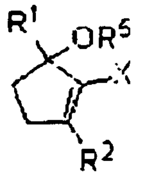
R^5-Y (VI)

[0023] In the Formulae, R^1, R^2, R^5 and X are the same as defined in the Formulae I-VIII.

[0024] Further, a method of preparing the compound of Formula VIII from the compound of the Formula IX, and a method of preparing the fulvene compound of the Formula VIII from the compound of the Formula VII are disclosed.

[0025] The method of preparing the compound of the Formula VII from the compound of the Formula IX comprises

a) lithiating the compound of the Formula IX, or converting the compound with a Grignard reagent, and then reacting the resulting organanetallic compound with an electrophile of Formula IV below to prepare a compound of Formula X below; and



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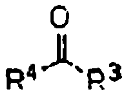

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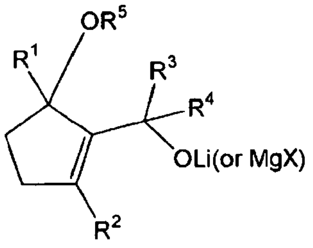
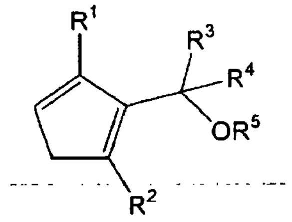


(X)

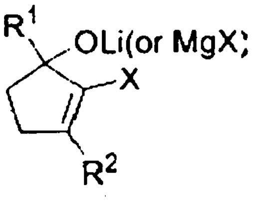
b) reacting more than one equivalent of the compound of the Formula X with a compound of Formula VI below to prepare an ether, and then dehydrating with an acid catalyst to prepare a compound of Formula VIII below

$R^5 - Y$ (VI)



(VII).

[0026] Further, the present invention provides a method of preparing a compound of Formula XI below, which is a precursor of a metallocene compound having substituents only at the α -positions with respect to the bridging point of a 5-membered cyclopentadienyl ring, comprising lithiating the compound of the Formula III or the compound of the Formula IX, or converting the compounds with a Grignard reagent, and then reacting the resulting organometallic compounds with the compound of the Formula VIII below, and then treating with an acid:



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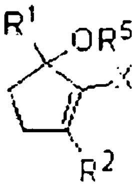

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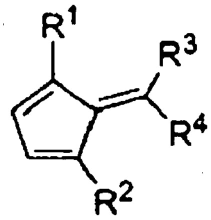

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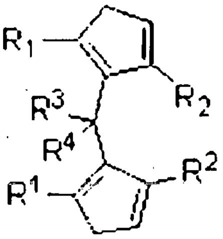
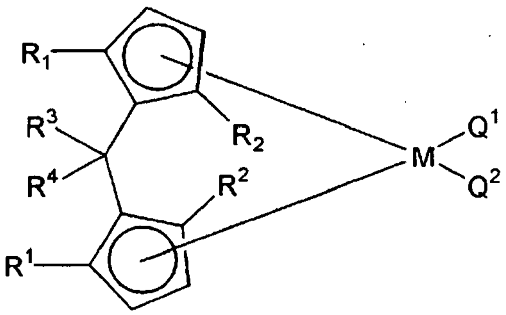


(XI).

[0027] The method of preparing a compound of Formula XII below, which is a metallocene compound having substituents only at the α-positions with respect to the bridging point of a 5-membered cyclopentadienyl ring, from the compound of the Formula XI can follow the method described in various literatures regarding the preparation of a metallocene compound in ansa-form from a compound in which two 5-membered cyclopentadienyl rings are bridged:



(XII).

[0028] In the Formula XI and XII, each of R^1, R^2, R^3 and R^4 is independently or simultaneously a hydrogen atom; a C_1-C_{20} alkyl or aryl comprising optionally an oxygen atom; or a C_1-C_{20} alkenyl, alkylaryl or arylalkyl, and

[0029] R^1 is not a hydrogen atom, and R^3 and R^4 can be connected together by an alkylidene radical comprising a C_1-C_{20} alkyl or aryl radical to form a ring.

[0030] In the MQ^1Q^2, Q^1 and Q^2 are each independently or simultaneously a halogen atom; a C_1-C_{20} alkyl, alkenyl, alkylaryl or arylalkyl; an aryl; a substituted or unsubstituted C_1-C_{20} alkylidene; a substituted or unsubstituted amido group; a C_1 -C_{20} alkylalkoxy; or an arylalkoxy; and M is a Group IV metal.

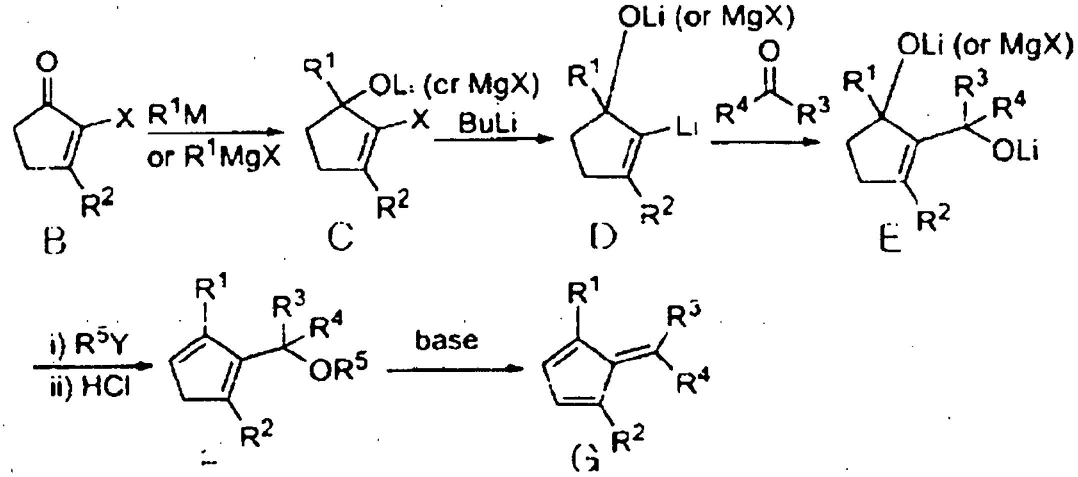
[0031] The method of preparing the compound of the Formula XII from the compound of the Formula XI includes a method that the compound of the Formula XI is treated with a strong base, such as KH, Mg and alkyl lithium, to form a divalent anion, and then reacted with a metal compound comprising at least two halogen atoms per a metal element, thereby obtaining the compound of the Formula XII. See H. Wiesenfeldt et al, J. Organomet. Chem., 369 359 (1989), S. Gutmann et al, J. Organomet. Chem., 369 343 (1989), and S. Collins et al, Organometallics, 9 2695 (1990). Another method includes a method that the divalent anion formed by treating the compound of the Formula XI with a strong base is reacted with a Group XIV metalloid organic metal compound comprising at least one halogen element to substitute each 5-membered ring with a metalloid element, and then reacted with a metal compound comprising at least two halogen atoms per a metal element, thereby obtaining the compound of the Formula XII. See Bunyeoul Lee et al, J. Organomet. Chem., 660 161 (2002). Still another method includes a method that the compound of the Formula XI is used as such without treating with a base, and reacted with a metal amido compound, as described in U.S. Patent No. 5,998,643. According to the most preferable method of these methods, the compound of the Formula XI is treated with 2 equivalents of n-butyl lithium to dehydrogenate each 5-membered cyclopentadienyl ring, thereby forming a divalent anion, and by the reaction of the divalent anion with a metal halide compound, etc., a bridged metallocene compound comprising a cyclopentadienyl group containing one carbon at bridge position and a substituent only at α position can be prepared.

[0032] Hereinafter, the present invention is described in more detail.

[0033] The present invention provides a method of preparing 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compounds. Further, the present invention relates to a method of preparing an ansa-metallocene compound in which two cyclopentadienyl ligands are bridged by one carbon and there is a substituent only at positions adjacent to the bridging point of a cyclopentadienyl ligand, using the fulvene compound.

[0034] A method of preparing the fulvene compound of the Formula VIII follows the Reaction Scheme VI below.

Reaction Scheme VI

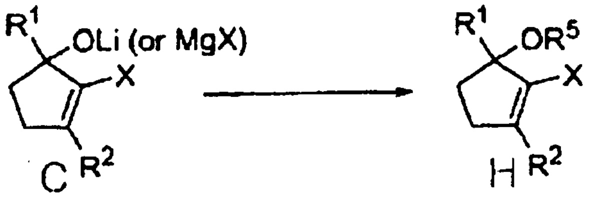


[0035] In the Reaction Scheme VI, R^1-R^5 are the same as defined above. In the starting material compound B (Formula I), X is a halogen atom including I, Br or Cl, preferably Br or I. The compound that X is Br is mass-producible by previously known methods (J. Organomet. Chem. , 677(2003), 133). The compound that X is I is also mass-producible by previously known methods (Tetrahedron Lett., 33(1992), 917) . In the Reaction Scheme VI, nucleophilic attack of the organometallic compounds of the Formulae IIa or IIb to the compound B where X is Br affords an anionic compound C (Fomula III) of a tertiary alcohol, and subsequently alkyl lithium is added at a low temperature in the identical reactor to prepare the lithium salt (compound D). The lithium salt is reacted with an electrophile of the Formula IV to obtain a dilithium salt (compound E). Herein, the form of R^3 and R^4 can be defined by the structure of the electrophile. When the compound, such as an alkyl halide or an alkyl sulfonate, according to the Formula VI is added in the same equivalent to the compound E (Formula V), the oxo anion attached on the carbon, to which R^3 and R^4 are also attached, is converted to an ether group. When two equivalents of the compound according to the Formula VI are used, the oxo anion attached on the carbon substituted with R^1, is also converted to an ether group. At this reaction step, the oxo anions attached on the carbons substituted with R^1 need not be necessarily converted to ethers, however, it is preferable that the oxo anions are all converted to ethers. Finally, when an acid is added, the OH or alkoxy group attached on the carbon substituted with R^1 is eliminated as water or an alcohol with the hydrogen atom attached on an adjacent carbon, and thus a double bond is formed, thereby obtaining the compound F (Formula VII) of the Reaction Scheme VI. The compound can be used after purification by the vacuum distillation or chromatography, or can be also used in next reaction without purification. If the compound F (Formula VII) is treated with a base in various solvents, desired fulvene compound G (Formula VIII) can be obtained.

[0036] Preferably, the compound F can be obtained by sequentially adding reactants in one reactor without isolating and purifying intermediate compounds C, D and E from the compound B. However, the procedure of the isolation and purification of the intermediates may be performed in various ways. For example, the compound D may be prepared by adding water to the compound C to form an alcohol, purifying it, and then adding the excessive butyl lithium. In addition, the compound F may be prepared by adding water to the compound E to convert to an alcohol, isolating and purifying it, protecting the alcohol in various ways, and then treating with an acid. The compound F may be prepared by adding water to the compound E to convert to an alcohol, dehydrating by treating with an acid to obtain a cyclopentadienyl compound, and then protecting the rest of the alcohol. Further, if desired, the compounds C, D and E can be also used after purification with various ways.

[0037] The compound according to the Formula IX, which can be used as an intermediate in preparing the ansa-metallocene compound in which two cyclopentadienyl ligands are bridged by one carbon and there are substituents only at positions adjacent to the bridging point of two cyclopentadienyl ligands, can be prepared by Reaction Scheme VII below. That is, when the compound of the Formula VI is reacted with the compound of the Formula III, which is an intermediate in preparing a fulvene, the compound H (Formula IX) of the Reaction Scheme VII below is obtained. Further, the compound H (Formula IX) can be also obtained by adding water to the compound C (Formula III), isolating and purifying it to obtain an alcohol compound, and then protecting the alcohol functional group. The method of protecting an alcohol group by converting to an ether compound such that the alcohol group can be stable under subsequent organometallic reaction condition include well-known organic synthetic methods, such as the method of substituting the hydrogen atom of an alcohol with an alkyl group, the method of substituting the hydrogen atom of an alcohol with an alkoxyalkyl group, or the method of protecting by insertion to a cycloalkene compound. Such protecting method of an alcohol is well described in' Protective Groups in Organic Synthesis', 3rd Ed. (T.W. Green 1999).

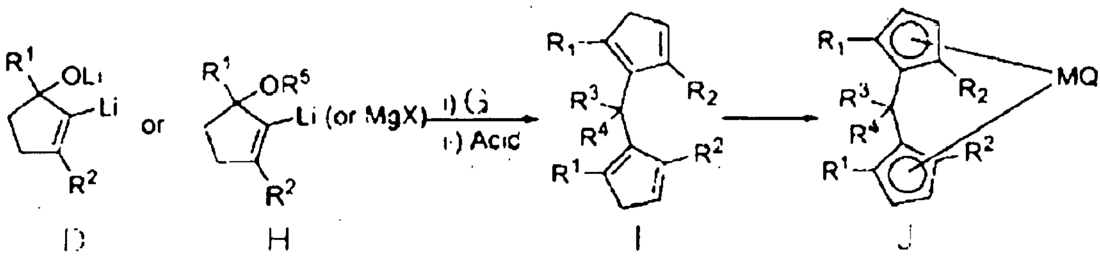
Reaction Scheme VII



[0038] The fulvene compound according to the Formula VIII can be also prepared by using the compound H (Formula IX) of the Reaction Scheme VII. In the method, the fulvene compound can be prepared via the same reaction step by using the compound H (Formula IX) of the Reaction Scheme VII instead of the compound C. When the compound H (Formula IX) is used instead of the compound C (Formula III), lithium metal can be used instead of expensive butyl lithium to generate lithium salt, or the compound H can be converted with the Grignard reagent instead of making lithium salt, and then the resulting product can be reacted with the compound of the Formula IV to prepare the intermediate compound according to the Formula X. Then, subsequent reaction can be proceeded to obtain desired object.

[0039] The ansa-metallocene compound in which two cyclopentadienyl ligands are bridged by one carbon and there are substituents only at positions adjacent to the bridging point of two cyclopentadienyl ligands, can be prepared by Reaction Scheme VIII below. The ligand compound I (Formula XI) is obtained by reacting the fulvene compound G (Fomula VIII) of the Reaction Scheme VI with a material produced by making lithium salt of the compound D (Formula III) prepared in the Reaction Scheme VI or the compound H (Formula IX) of the Reaction Scheme VII or converting them with the Grignard reagent, and then treating the resulting compound with an acid. A metallocene compound J (Formula XII) can be prepared from the compound I (Formula XI) by various known methods.

Reaction Scheme VIII



[0040] The present invention will be described in greater detail with reference to the following examples. The following examples are for illustrative purposes and are not intended to limit the scope of the invention.

Mode for Invention

[0041] The organic reagents and solvents were purchased from the Aldrich Company and Merck Company, and used after purification by a standard method. The reproducibility of an experiment was elevated by blocking the contact with air and moisture in all steps of preparation. The spectrum was obtained to verify the structure of a compound by using 400 MHz nuclear magnetic resonance spectrometer (NMR).

Example 1

Preparation of a 2-methoxymethyl-1,3-dimethyl-cyclopenta-1,3-diene [Formula VII (R^1, R^2 = CH_3 ; R^3, R^4 = H)]

[0042] 121.7 mℓ of 1.1 equivalents of methyl lithium solution was slowly added to 300 mℓ of tetrahydrofuran solution in which 29g (166 mmol) of 2-bromo-3-methyl-2-cyclopentene-1-one [Formula I (R^2 =CH_3, X = Br)] compound are dissolved at -78 °C nitrogen state, and then the mixture was reacted for 2 hours. 195.3 mℓ of 2.0 equivalents of tertiary butyl lithium solution was slowly added at the same temperature, and then the mixture was reacted for 2 hours. 3 equivalents of paraformaldehyde and the catalytic amount of paratoluenesulfonic anhydride were reacted at 100 °C, and then the resulting formaldehyde gas was introduced in a reaction flask. After the completion of introducing the formaldehyde gas, the solvent was removed under reduced pressure while slowly elevating the temperature to a room temperature. After the removal of the solvent, 250 mℓ of dimethylformanide was injected into the reaction vessel using a cannula. 2 equivalents of methyl iodide were added thereto and the mixture was reacted for 15 hours. Then one equivalent of sodium hydride and the same equivalents of methyl iodide were added, and the mixture was reacted for a day. After the completion of the reaction, 300 mℓ of water and 300 mℓ of a sodium chloride solution were added and the mixture was extracted with 600 mℓ of hexane and once again with 200 mℓ of hexane. An organic layer was washed three times with 200 mℓ of a sodium chloride solution and the solvent was removed with a rotatory evaporator, and then 300 mℓ of ethyl acetate was added. 200 mℓ of 2N HCl solution was added to the extracted organic layer, and the resulting mixture was vigorously shaked for 2 minutes. Water layer was removed and the organic layer was neutralized with 200 mℓ of a saturated sodium bicarbonate solution. Isolated organic layer was treated with magnesium sulfate to remove water, and then vacuum-distillated to give 14.2g of white 2-methoxymethyl-1,3-dimethyl-cyclopenta-1,3-diene. Yield: 62%.

[0043] ^{1}H NMR ($CDCl_3$): δ 5.83 (s, 1H, CH_2), 4.15 (s, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 2.85 (s, 2H, CH_2), 2.05 (s, 3H, CH_3), 1.99 (s, 3H, CH_3)ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.95, 142.81, 123.65, 65.73, 57.72, 44.36, 14.13, 13.92 ppm.

Example 2

[0044] Preparation of 1,4-demethyl fulvene [Formula VIII (R^1, R^2 = CH_3; R^3, R^4 = H)] 4.74 g (34.3 mmol) of the 2-methoxymethyl-1,3-dimethyl-cyclopenta-1,3-diene prepared in the example 1 were dissolved in 30 mℓ of pentane under nitrogen atmosphere, and one equivalent of sodium hydride was added at -20 °C, the mixture was reacted for 3 hours while slowly elevating the temperature. Then, the reactant was only filtered, without separate purification, to obtain a pentane solution, and the solution was used in next reaction. By isolating a portion of the product, 1,4-dimethyl fulvene compound could be confirmed.

[0045] ^{1}H NMR (C_6D_6): δ 5.95 (d, J=1.2Hz, 2H, CH), 5.41(t, J=1.2Hz, 2H, CH_2), 1.89 (d, J=1.2Hz, 6H, CH_3)ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 154.51, 131.17, 128.98, 114.71, 12.44 ppm.

Example 3

Preparation of 2-bromo-3-methoxy-1,3-dimethyl-cyclopentene [Formula IX (R^1, R^2, R^5=CH_3)]

[0046] 152 mℓ (0.228 mol) of methyl lithium solution was placed in 1L flask at nitrogen atmosphere, and then the solvent was removed under reduced pressure. Then 0.10L of tetrahydrofuran was injected, and then a solution in which 40g (0.228 mol) of 2-bromo-3-methyl-2-cyclopentene-1-one [Formula I (R^2 =CH_3, X = Br)] compound are dissolved in 0.1 L of tetrahydrofuran at -78 °C, was injected, and then the mixture was stirred for 1 hour. After 1 hour, the solvent was removed under reduced pressure, then 0.2L of dimethylformamide was added, and then one equivalent of methyl iodide was added with stirring. After reaction at 40 °C for 2 hours, one equivalent of sodium hydride was added and the same equivalent of methyl iodide was added, and the mixture was reacted at 40 °C for 15 hours. After the completion of the reaction, 400 mℓ of water was added and the organic layer extracted with 600 mℓ of hexane was washed three times with 200 mℓ of a sodium chloride solution, then the organic layer was dried with a sodium carbonate solution, and then the solvent was removed with a rotary evaporator, and then the vacuum distillation was performed at 67 Pa (500mTorr), 50 °C to give 32.7g of 2-bromo-3-methoxy-1,3-dimethyl-cyclopentene compound. Yield: 79%.

[0047] ^{1}H NMR ($CDCl_3$): δ 3.11 (s, 3H, OCH_3), 2.42-2.24 (m, 2H, CH_2), 2.18 (ddd, J=14.0, 4.0, 9.2Hz, 1H, CH_2), 1.92 (ddd, J=14.4, 5.6, 9.2Hz, 1H, CH_2), 1.82 (s, 3H, CH_3)ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.49, 121.78, 88.35, 50.30, 34.83, 31.98, 26.34, 16.37ppm.

Example 4

Preparation of 2,2'-methylenebis(1,3-dimethyl-l,3-cyclopentadien) [Formula XI (R^1 , R^2 = CH_3 ; R^3, R^4 = H)]

[0048] One equivalent of n-butyl lithium was added to a solution in which 7.038g (34.3mmol) of 2-bromo-3-methoxy-1,3-dimethyl-cyclopentene compound prepared in the example 3 was dissolved in 38 mℓ of ether at -25 °C nitrogen atmosphere. When white solid was precipitated, the temperature was elevated to 10 °C and the reaction was continued for further 10 minutes. The temperature was lowered to -25 °C and the fulvene compound prepared in the example 2 was added. Completion of reaction is determined by the development of yellow color of the reaction mixture. 50 mℓ of water was added to the reaction mixture and the solvent was removed using the rotatory evaporator. 50 mℓ of 2N HCl solution was added to the organic layer extracted with 50 mℓ of ethyl acetate, and the resulting mixture was vigorously shaked for 2 minutes. Water layer was removed by layer separation and the organic layer was neutralized with 50 mℓ of a saturated sodium bicarbonate solution. Isolated organic layer was dried over magnesium sulfate, and then the vacuum distillation was performed to give 4.17g of yellow 2,2'-methylenebis(1,3-dimethyl-1,3-cyclopentadiene) compound. Yield: 61%.

Example 5

Preparation of 2,2'-methylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride [Formula XII (R^1,R^2 = CH_3 ; R^3, R^4 = H)]

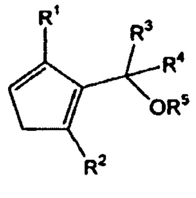
[0049] Two equivalents of n-butyl-lithium were added to a solution in which 3.24g (16.17mmol) of 2,2'-methylenebis(1,3-dimethyl-1,3-cyclopentadiene) compound prepared in the example 4 was dissolved in 40 mℓ of diethyl ether at -78 °C nitrogen atmosphere, and the mixture was reacted for a day with slowly warming to room temperature. The solid filtered under nitrogen atmosphere was washed twice with 20 mℓ of diethyl ether, and then the solvent was removed completely under reduced pressure. 200g (0.853 mmol) of lithium salt thus made were dissolved in a mixed solvent containing 15 mℓ of toluene and 3 of tetrahydrofuran. The same equivalent of zirconium tetrachloride compound was added, the mixture was reacted for a day, and then the reactants were filtered, and the solvent of the filtered solution was removed under reduced pressure to give 263 mg of pale yellow solid compound. Yield: 85%.

[0050] As described above, the present invention provides a simple method of preparing 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compounds. The method described in the present invention has shorter preparation step and is mass-producible over the method described in prior invention (Korean Patent Application No. 10-2002-51425). Further, the present invention also provides a simple method of preparing an ansa-metallocene compound in which two cyclopentadienyl ligands are bridged by one carbon and there are substituents only at positions adjacent to the bridging point of cyclopentadienyl ligand. Prior art method needed high pressure of carbon monoxide and a temperature higher than 400 °C. Prior art method has long reaction steps and must isolate and purify an intermediate by chromatography method, and thus has a problem in mass production. However, the method of the present invention overcomes such a problem and is easily mass-producible.

[0051] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein within the scope defined by the following claims.

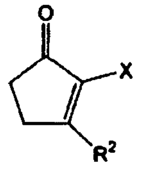
Claims

1. A method of preparing the compound of Formula VII below comprising



(VII)

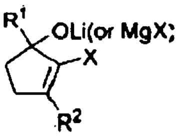
a) reacting Formula I below with a compound of Formula IIa or IIb below to prepare a compound of Formula III below;



(I)

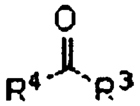
R^1-Li (IIa)

R^1-MgX (IIb)

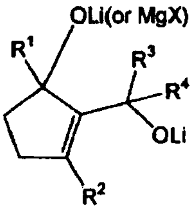


(III)

b) lithiating the compound of the Formula III, and then reacting the resulting lithium salt with an electrophile of Formula IV below to prepare a compound of Formula V below; and



(IV)



(V)

c) reacting the compound of the Formula V with more than one equivalent of a compound of Formula VI below to prepare an ether, and then dehydrating with an acid catalyst to prepare a compound of Formula VII

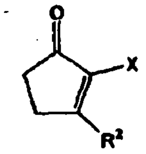
R^5-Y (VI)

wherein R^1, R^2, R^3 and R^4 are each independently or simultaneously a hydrogen atom; a C_1-C_{20} alkyl or aryl comprising optionally an oxygen atom; or a C_1-C_{20}alkenyl, alkylaryl or arylalkyl, and
R^1 is not a hydrogen atom, and R^3 and R^4 can be connected together by an alkylidene radical comprising a C_1-C_{20} alkyl or aryl radical to form a ring;

X is a halogen atom;
R^5 is a C_1-C_{20} alkyl, alkenyl, alkylaryl, or a radical of Group XIV metal substituted with an arylalkyl, an aryl, an alkoxyalkyl or a hydrocarbyl;
Y is a leaving group formed by a nucleophilic substitution reaction.

2. A method according to claim 1 of preparing a 1,4,6-substituted, 1,4-substituted, 1,6-substituted, or 1-substituted fulvene compound comprising

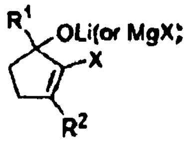
a) reacting Formula I below with a compound of Formula IIa or IIb below to prepare a compound of Formula III below;



(I)

R^1-Li (IIa)

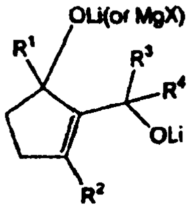
R^1-MgX (IIb),



(III)

b) lithiating the compound of the Formula III, and then reacting the resulting lithium salt with an electrophile of Formula IV below to prepare a compound of Formula V below;

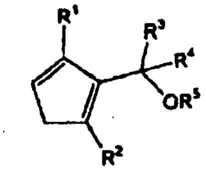
(IV)



(V)

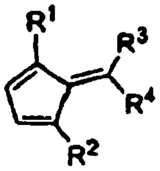
c) reacting the compound of the Formula V with more than one equivalent of a compound of Formula VI below to prepare an ether, and then dehydrating with an acid catalyst to prepare a compound of Formula VII below; and

R^5-Y (VI)



(VII)

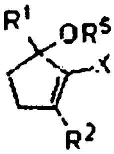
d) adding a base to the compound of the Formula VII to prepare a fulvene compound of Formula VIII



(VIII)

wherein R^1, R^2, R^3, R^4, R^5, X and Yare the same as defined in claim 1.

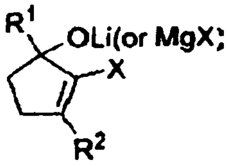
3. A compound of Formula IX below:



(IX)

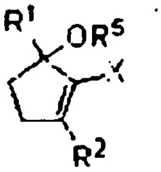
wherein R^1, R^2, R^5 and X are the same as defined in claim 1.

4. A method of preparing a compound of Formula IX below comprising reacting the compound of the Formula III with a compound of Formula VI below to prepare a compound of the Formula IX:



(III)

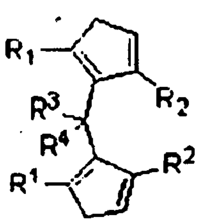
R^5-Y (VI)



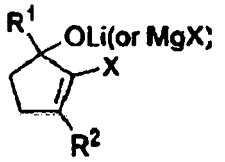
(IX)

wherein R^1, R^2, R^5, X and Y are the same as defined in claim 1.

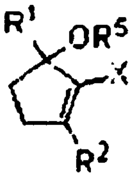
5. A method of preparing a compound of Formula XI below comprising lithiating the compound of Formula III below or the compound of Formula IX below, or converting the compounds with a Grignard reagent, and then reacting the resulting organometallic compounds with the compound of the Formula VIII below, and then treating with an acid:



(XI)



(III)



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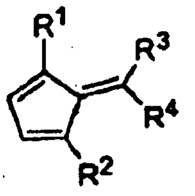
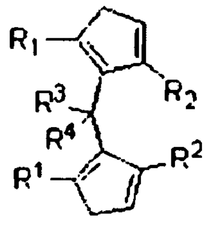


(VIII)

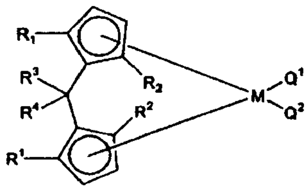
wherein R^1, R^2, R^3, R^4, R^5 and X are the same as defined in claim 1.

6. A method according to claim 5 of preparing a compound of Formula XII from a compound of Formula XI below,

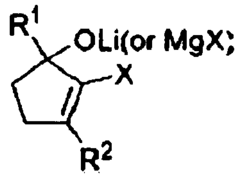
characterized in that the compound of the Formula XI is prepared by reacting a compound of Formula III below or a compound of Formula IX below with lithium metal or converting the compounds with a Grignard reagent, reacting with a compound of Formula VIII below, and then treating with an acid:



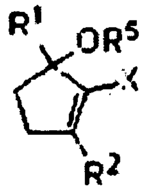
(XI)



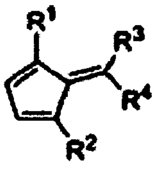
(XII)



(III)



(IX)



(VIII)

wherein

R^1, R^2, R^3, R^4, R^5 and X are the same as defined in claim 1,
Q^1 and Q^2 are each independently or simultaneously a halogen atom; a C_1-C_{20} alkyl, alkenyl, alkylaryl or arylalkyl ; an aryl; a substituted or unsubstituted C_1-C_{20} alkylidene; a substituted or unsubstituted amido group; a C_1-C_{20} alkylalkoxy;
or an arylalkoxy; and
M is a Group IV metal.

7. The method of claim 1 or 2, wherein the compound of the Formula I is selected from the group consisting of 2-bromo-2-cyclopentene-1-one, 2-bromo-3-methyl-2-cyclopentene-1-one and 2-iodo-3-methyl-2-cyclopentene-1-one.

8. The method of any one of claims 1 or 2, wherein the compound of the Formula IV is selected from the group consisting of acetone, formaldehyde, acetaldehyde, benzaldehyde, benzophenone, methylethylketone, butyraldehyde and propionaldehyde.

9. The method of any one of claims 1, 2, 4, 5, or 6, wherein R^1 and R^2 are both methyl.

10. The method of any one of claims 1, 2, 5, or 6, wherein R^1 and R^2 are both methyl, R^3 is a hydrogen atom, R^4 is a hydrogen atom, methyl or phenyl.

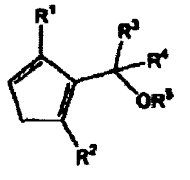
11. The method of any one of claims 1, 2, 4, 5 or 6, wherein R^1, R^2 and R^5 are all methyl, and X is bromine.

12. The method of any one of claims 1, 2, 5 or 6, wherein R^1 and R^2 are both methyl, R^3 and R^4 are both hydrogen atom.

13. The compound of claim 3, wherein R^1 and R^2 are both methyl.

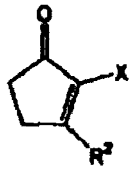
Patentansprüche

1. Verfahren zur Herstellung der Verbindung der Formel VII unten umfassend



(VII)

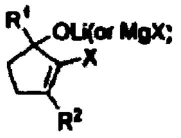
a) in Reaktion bringen von Formel I unten mit einer Verbindung der Formel IIa oder IIb unten, um eine Verbindung der Formel III unten herzustellen;



(I)

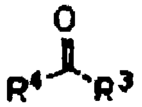
R^1-Li (IIa)

R^1-MgX (IIb)

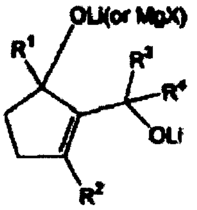


(III)

b) Lithiieren der Verbindung der Formel III und anschließend in Reaktion bringen des resultierenden Lithiumsalzes mit einem Elektrophil der Formel IV unten, um eine Verbindung der Formel V unten herzustellen; und



(IV)



(V)

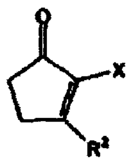
c) in Reaktion bringen der Verbindung der Formel V mit mehr als einem Äquivalent einer Verbindung der Formel VI unten, um einen Ether herzustellen und anschießend Dehydratisieren mit einem Säurekatalysator, um eine Verbindung der Formel VII herzustellen

R^5-Y (VI)

wobei R^1, R^2, R^3 und R^4 jeweils unabhängig oder gleichzeitig ein Wasserstoffatom; ein C_1-C_{20} Alkyl oder Aryl optional ein Sauerstoffatom umfassend; oder ein C_1-C_{20} Alkenyl, Alkylaryl oder Arylalkyl sind, und R^1 kein Wasserstoffatom ist, und R^3 und R^4 durch ein Alkylidenradikal, welches ein C_1-C_{20} Alkyl oderArylradikal umfasst, miteinander verbunden sein können, um einen Ring zu bilden;
X ein Halogenatom ist,
R^5 ein C_1-C_{20} Alkyl, Alkenyl, Alkylaryl oder ein Radikal von Gruppe XIV Metall ist, welches mit einem Arylalkyl, einem Aryl, einem Alkoxyalkyl oder einem Hydrocarbyl substituiert ist; Y eine Abgangsgruppe ist, welche durch eine nukleophile Substitutionsreaktion gebildet wird.

2. Verfahren nach Anspruch 1 zur Herstellung einer 1,4,6-substituierten, 1,4-substituierten, 1,6-substituierten oder 1-substituierten Fulvenverbindung umfassend

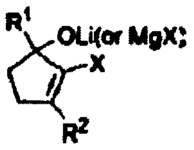
a) in Reaktion bringen der Formel I unten mit einer Verbindung der Formel IIa oder IIb unten, um eine Verbindung der Formel III unten herzustellen;



(I)

R^1-Li (IIa)

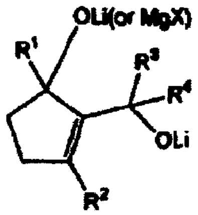
R^1-MgX (IIb),



(III)

b) Lithiieren der Verbindung der Formel III und anschließend in Reaktion bringen des resultierenden Lithiumsalzes mit einem Elektrophil der Formel IV unten, um eine Verbindung der Formel V unten herzustellen;

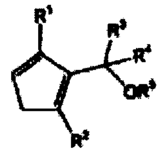
(IV)



(V)

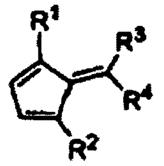
c) in Reaktion bringen der Verbindung der Formel V mit mehr als einem Äquivalent einer Verbindung der Formel VI unten, um einen Ether herzustellen und anschließend Dehydratisieren mit einem Säurekatalysator, um eine Verbindung der Formel VII unten herzustellen; und

R^5-Y (VI)



(VII)

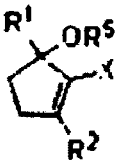
d) Zugeben einer Base zu der Verbindung der Formel VII, um eine Fulvenverbindung der Formel VIII herzustellen



(VIII)

wobei R^1, R^2, R^3, R^4, R^5, X und Y sind die Gleichen wie in Anspruch 1 definiert.

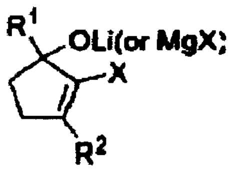
3. Verbindung der Formel IX unten:



(IX)

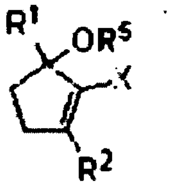
wobei R^1, R^2, R^5 und X sind die Gleichen wie in Anspruch 1 definiert.

4. Verfahren zur Herstellung einer Verbindung der Formel IX unten, umfassend in Reaktion bringen der Verbindung der Formel III mit einer Verbindung der Formel VI unten, um eine Verbindung der Formel IX herzustellen:



(III)

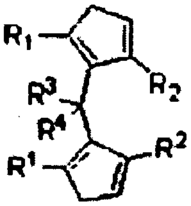
R^3-Y (VI)



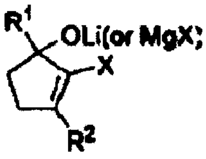
(IX)

wobei R^1, R^2, R^5, X und Y sind die Gleichen wie in Anspruch 1 definiert.

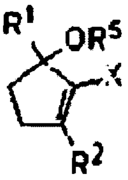
5. Verfahren zur Herstellung einer Verbindung der Formel XI unten umfassend Lithiieren der Verbindung der Formel III unten oder der Verbindung der Formel IX unten oder Umsetzen der Verbindung mit einem Grignardreagenz und anschließend in Reaktion bringen der resultierenden organometallischen Verbindung mit der Verbindung der Formel VIII unten und anschließend Behandeln mit einer Säure:



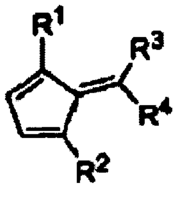
(XI)



(III)



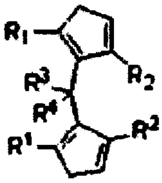
(IX)



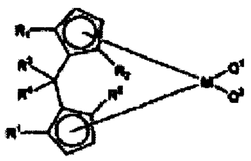
(VIII)

wobei R^1, R^2, R^3, R^4, R^5 und X sind die Gleichen wie in Anspruch 1 definiert.

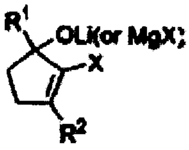
6. Verfahren nach Anspruch 5 zur Herstellung einer Verbindung der Formel XII von einer Verbindung der Formel XI unten, dadurch charakterisiert, dass die Verbindung der Formel XI hergestellt wird durch in Reaktion bringen einer Verbindung der Formel III unten oder einer Verbindung der Formel IX unten mit Lithiummetall oder Umsetzen der Verbindungen mit einem Grignardreagenz, in Reaktion bringen mit einer Verbindung der Formel VIII unten, und anschließend Behandeln mit einer Säure:



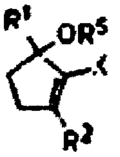
(XI)



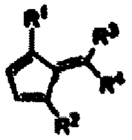
(XII)



(III)



(IX)



(VIII)

wobei

R^1, R^2, R^3, R^4, R^5 und X sind die Gleichen wie in Anspruch 1 definiert,

Q^1 und Q^2 jeweils unabhängig oder gleichzeitig ein Halogenatom; ein C_1-C_{20} Alkyl, Alkenyl, Alkylaryl oder Arylalkyl; ein Aryl; ein substituiertes oder unsubstituiertes C_1-C_{20}Alkyliden; eine substituierte oder unsubstituierte Amidogruppe; ein C_1-C_{20} Alkylalkoxy;
oder ein Arylalkoxy sind; und
M ein Gruppe IV Metall ist.

7. Verfahren nach Anspruch 1 oder 2, wobei die Verbindung der Formel I ausgewählt ist aus der Gruppe bestehend aus 2-Brom-2-cyclopenten-1-on, 2-Brom-3-methyl-2-cyclopenten-1-on und 2-Iod-3-methyl-2-cyclopenten-1-on.

8. Verfahren nach einem der Ansprüche 1 oder 2, wobei die Verbindung der Formel IV ausgewählt ist aus der Gruppe bestehend aus Aceton, Formaldehyd, Acetaldehyd, Benzhaldehyd, Benzophenon, Methylethyketon, Butyraldehyd und Propionaldehyd.

9. Verfahren nach einen der Ansprüche 1, 2, 4, 5 oder 6, wobei R^1 und R^2 beide Methyl sind.

10. Verfahren nach einem der Ansprüche 1, 2, 5 oder 6, wobei R^1 und R^2 beide Methyl sind, R^3 ein Wasserstoffatom ist, R^4 ein Wasserstoffatom, Methyl oder Phenyl ist.

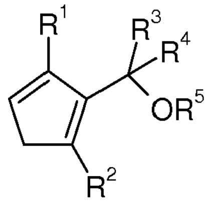
11. Verfahren nach einem der Ansprüche 1, 2, 4, 5 oder 6, wobei R^1, R^2 und R^5 alle Methyl sind und X Brom ist.

12. Verfahren nach einem der Ansprüche 1, 2, 5 oder 6, wobei R^1 und R^2 beide Methyl sind, R^3 und R^4 beide Wasserstoffatome sind.

13. Verbindung nach Anspruch 3, wobei R^1 und R^2 beide Methyl sind.

Revendications

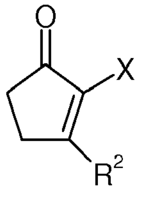
1. Procédé de préparation d'un composé de formule VII donnée ci-dessous :



(VII)

lequel procédé comporte les étapes suivantes :

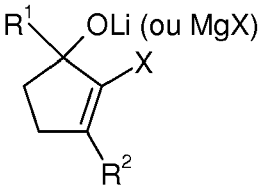
a) faire réagir un composé de formule I donnée ci-dessous avec un composé de formule IIa ou IIb donnée ci-dessous, de manière à préparer un composé de formule III donnée ci-dessous ;



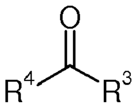
(I)

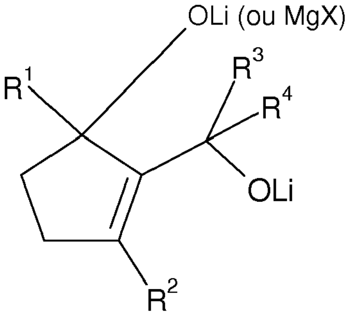
R^1-Li (IIa)

R^1-MgX (IIb)


(III)

b) soumettre le composé de formule III à une lithiation, puis faire réagir le sel de lithium résultant avec un électrophile de formule IV donnée ci-dessous, de manière à préparer un composé de formule V donnée ci-dessous ;


(IV)


(V)

c) et faire réagir ce composé de formule V avec plus d'un équivalent d'un composé de formule VI donnée ci-dessous, de manière à préparer un éther, qu'on soumet ensuite à une déshydratation, à l'aide d'un catalyseur acide, de manière à préparer un composé de formule VII ;

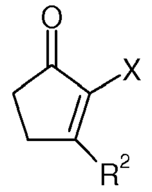
R^5-Y (VI)

étant entendu que :

- R^1, R^2, R^3 et R^4 représentent chacun, indépendamment ou simultanément, un atome d'hydrogène, un groupe alkyle en C_1-C_{20} ou aryle, en option comportant un atome d'oxygène, ou un groupe alcényle en C_1-C_{20}, alkyl-aryle ou aryl-alkyle,
étant entendu que R^1 ne représente pas un atome d'hydrogène et que les entités représentées par R^3 et R^4 peuvent être raccordées par un groupe alkylidène comportant un groupe alkyle en C_1-C_{20} ou aryle, de manière à former un cycle ;
- X représente un atome d'halogène ;
- R^5 représente un groupe alkyle en C_1-C_{20}, alcényle ou alkyl-aryle, ou un groupe formé par un atome d'un métal du groupe XIV portant un substituant aryl-alkyle, aryle, alcoxy-alkyle ou hydrocarbyle ;
- et Y représente un groupe partant formé lors d'une réaction de substitution nucléophile.

2. Procédé, conforme à la revendication 1, de préparation d'un composé de type fulvène porteur de substituant(s) en positions 1, 4 et 6, en positions 1 et 4, en positions 1 et 6 ou en position 1, lequel procédé comporte les étapes suivantes :

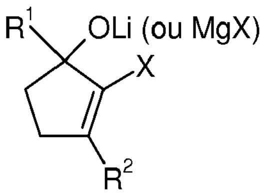
a) faire réagir un composé de formule 1 donnée ci-dessous avec un composé de formule IIa ou IIb donnée ci-dessous, de manière à préparer un composé de formule III donnée ci-dessous ;



(I)

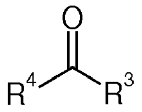
R^1-Li (IIa)

R^1-MgX (IIb)

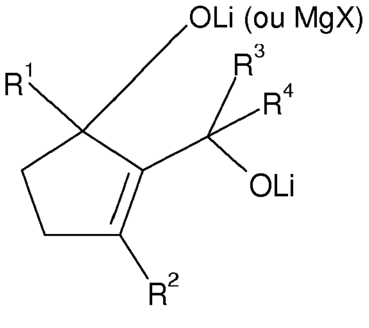


(III)

b) soumettre le composé de formule III à une lithiation, puis faire réagir le sel de lithium résultant avec un électrophile de formule IV donnée ci-dessous, de manière à préparer un composé de formule V donnée ci-dessous ;



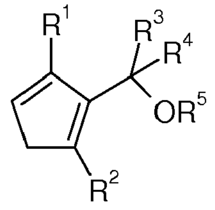
(IV)



(V)

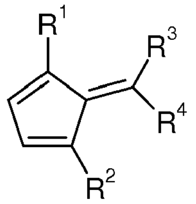
c) faire réagir ce composé de formule V avec plus d'un équivalent d'un composé de formule VI donnée ci-dessous, de manière à préparer un éther, qu'on soumet ensuite à une déshydratation, à l'aide d'un catalyseur acide, de manière à préparer un composé de formule VII donnée ci-dessous ;

R^5-Y (VI)



(VII)

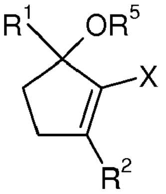
d) et ajouter une base à ce composé de formule VII, de manière à préparer un composé de type fulvène, de formule VIII donnée ci-dessous ;



(VIII)

étant entendu que les symboles R^1, R^2, R^3, R^4, R^5, X et Y ont les mêmes significations que celles indiquées dans la revendication 1.

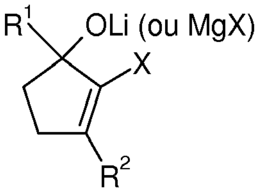
3. Composé de formule IX donnée ci-dessous :



(IX)

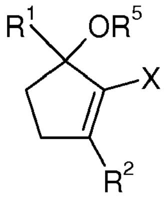
dans laquelle les symboles R^1, R^2, R^5 et X ont les mêmes significations que celles indiquées dans la revendication 1.

4. Procédé de préparation d'un composé de formule IX donnée ci-dessous, qui comporte le fait de faire réagir un composé de formule III avec un composé de formule VI donnée ci-dessous, de manière à préparer un composé de formule IX :



(III)

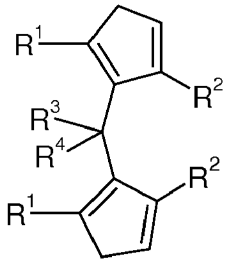
R^5-Y (VI)



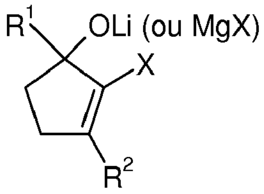
(IX)

étant entendu que les symboles R^1, R^2, R^5, X et Y ont les mêmes significations que celles indiquées dans la revendication 1.

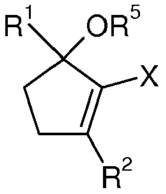
5. Procédé de préparation d'un composé de formule XI donnée ci-dessous, qui comporte le fait de soumettre à une lithiation un composé de formule III donnée ci-dessous ou un composé de formule IX donnée ci-dessous, ou le fait de convertir l'un de ces composés avec un réactif de Grignard, et le fait de faire ensuite réagir le composé organométallique résultant avec un composé de formule VIII donnée ci-dessous, puis le fait d'effectuer un traitement avec un acide :



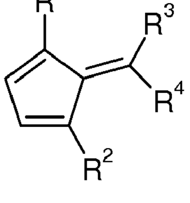
(XI)



(III)



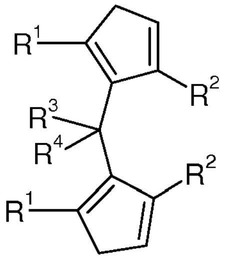
(IX)



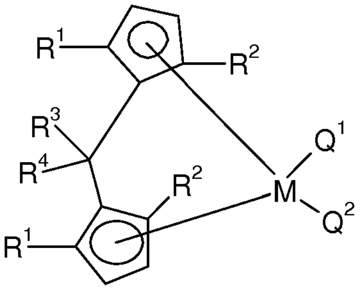
(VIII)

étant entendu que les symboles R^1, R^2, R^3, R^4, R^5 et X ont les mêmes significations que celles indiquées dans la revendication 1.

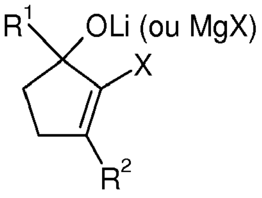
6. Procédé, conforme à la revendication 5, de préparation d'un composé de formule XII à partir d'un composé de formule XI donnée ci-dessous, **caractérisé en ce qu'**on prépare le composé de formule XI par réaction d'un composé de formule III donnée ci-dessous ou d'un composé de formule IX donnée ci-dessous avec du lithium à l'état de métal, ou par conversion de l'un de ces composés avec un réactif de Grignard, et réaction avec un composé de formule VIII donnée ci-dessous, puis traitement avec un acide :



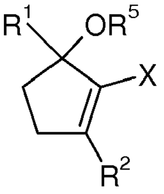
(XI)



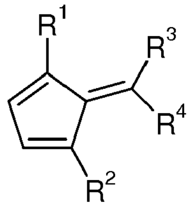
(XII)



(III)



(IX)



(VIII)

étant entendu que

- les symboles R^1, R^2, R^3, R^4, R^5 et X ont les mêmes significations que celles indiquées dans la revendication 1,
- Q^1 et Q^2 représentent chacun, indépendamment ou simultanément, un atome d'halogène, un groupe alkyle en C_1-C_{20}, alcényle, alkyl-aryle ou aryl-alkyle, un groupe aryle, un groupe alkylidène en C_1-C_{20} avec ou sans substituant(s), un groupe amido avec ou sans substituant(s), un groupe alkyl-alcoxy en C_1-C_{20}, ou un groupe aryl-alcoxy ;
- et M représente un atome d'un métal du groupe IV.

7. Procédé conforme à la revendication 1 ou 2, dans lequel le composé de formule I est choisi dans l'ensemble formé par les suivants : 2-bromo-cyclopent-2-ène-1-one, 2-bromo-3-méthyl-cyclopent-2-ène-1-one, et 2-iodo-3-méthyl-cyclopent-2-ène-1-one.

8. Procédé conforme à la revendication 1 ou 2, dans lequel le composé de formule IV est choisi dans l'ensemble formé par les suivants : acétone, formaldéhyde, acétaldéhyde, benzaldéhyde, benzophénone, méthyl-éthyl-cétone, butyraldéhyde et propionaldéhyde.

9. Procédé conforme à l'une des revendications 1, 2, 4, 5 et 6, dans lequel les deux symboles R^1 et R^2 représentent chacun un groupe méthyle.

10. Procédé conforme à l'une des revendications 1, 2, 5 et 6, dans lequel les deux symboles R^1 et R^2 représentent chacun un groupe méthyle, R^3 représente un atome d'hydrogène, et R^4 représente un atome d'hydrogène ou un groupe méthyle ou phényle.

11. Procédé conforme à l'une des revendications 1, 2, 4, 5 et 6, dans lequel tous les symboles R^1, R^2 et R^5 représentent chacun un groupe méthyle, et X représente un atome de brome.

12. Procédé conforme à l'une des revendications 1, 2, 5 et 6, dans lequel les deux symboles R^1 et R^2 représentent chacun un groupe méthyle, et les deux symboles R^3 et R^4 représentent chacun un atome d'hydrogène.

13. Composé conforme à la revendication 3, dans lequel les deux symboles R^1 et R^2 représentent chacun un groupe méthyle.

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