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(54) Title: SYNTHESIS OF 4-KETOCYCLOPENTENE AND CYCLOPENTADIENE COMPOUNDS		
(57) Abstract		
<p>A process for forming 4-ketocyclopentene and substituted 4-ketocyclopentene compounds starting from the corresponding 1-carbohydroxy-2-keto-4-hydroxy-5-cyclopentene by reduction followed by decarboxylation. The ketone may thereafter be converted to a cyclopentadiene compound by reducing the ketone to form an alcohol, replacing the hydroxyl functionality of the alcohol under substitution conditions with a leaving group, and deprotonating the resulting product under base induced elimination conditions to form the cyclopentadiene compound. Alternatively functionalized cyclopentadienyl compounds can be produced without isolation of an unsubstituted cyclopentadienyl compound by combining the elimination and deprotonation steps with a replacement step in a single unit operation.</p>		

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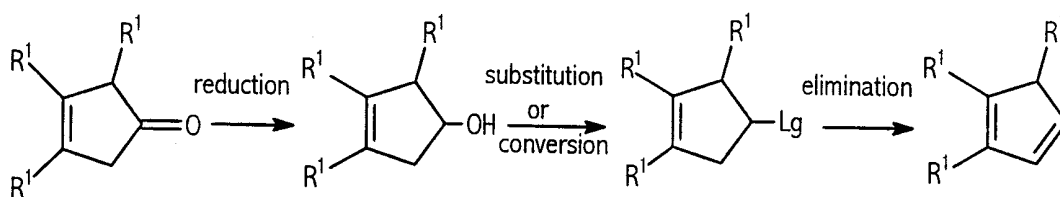
SYNTHESIS OF 4-KETOCYCLOPENTENE AND CYCLOPENTADIENE COMPOUNDS

This invention relates to the synthesis of 4-ketocyclopentene compounds including further substituted derivatives thereof, and their conversion to
5 cyclopentadiene compounds or substituted cyclopentadiene compounds, which are useful chemicals, particularly in the synthesis of cyclopentadienyl containing metal complexes useful in addition polymerization catalyst compositions. Group 4 metal complexes containing the foregoing cyclopentadienyl ligands are especially suited for use in catalyst compositions for the homopolymerization of ethylene or propylene and
10 the copolymerization of ethylene with an α -olefin. The present process is particularly suitable for use in the industrial scale preparation of 4-ketocyclopentene or substituted 4-ketocyclopentene compounds, cyclopentadiene or substituted cyclopentadiene derivatives thereof, and in the synthesis of cyclopentadienyl or substituted cyclopentadienyl containing metal complexes therefrom.

15 The preparation of cyclopentadiene compounds from various starting materials is well known. Metal complexes containing cyclopentadienyl or substituted cyclopentadienyl ligands are also well known. Several techniques for preparing such ligands are disclosed in US-A-5,703,187, US-A-4,985,576, US-A-5,646,083, US-A-5,597,935, and EP-A-563365. In copending application serial no. 8/122958,
20 filed July 27, 1998, the preparation of certain 1H-cyclopenta(/)phenanthrene containing metal complexes and their use in addition polymerization catalyst compositions is disclosed and claimed. The technique for preparing such complexes disclosed by the reference started with 1H-cyclopenta-(/)-phenanthrene. In JACS, 78, 2547-2551 (1956), a synthetic scheme for preparing 1H-cyclopenta(/)phenanthrene,
25 the ultimate step involving dehydration of 2,3-dihydro-2-oxo-1H-cyclopenta(/)phenanthrene with boric acid was disclosed. Disadvantageously, this particular procedure resulted in low yields and insufficient purity of the resulting ligand group containing compounds.

30 Previously known synthetic procedures involved multiple unit operations, thereby making the process less efficient than desired. Accordingly, it would be desirable if there were provided a process for preparing 4-ketocyclopentene or substituted 4-ketocyclopentene compounds and cyclopentadiene or substituted cyclopentadiene derivatives thereof in higher yields and purity.

35 According to the present invention there is provided a process for forming 4-ketocyclopentene and substituted 4-ketocyclopentene compounds starting from the corresponding 1-carbohydrocarbyloxy-2-keto-4-hydroxy-5-cyclopentene by reduction



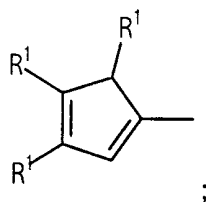
wherein R^1 is as previously defined, and

Lg is a suitable ligand group that is subject to base induced elimination.

- 5 Preferred Lg groups are: halo, silyl, OSO_2R^6 , $-\text{Si}(\text{R}^5)_2-$, $-\text{Si}(\text{R}^5)_2\text{N}(\text{R}^5)_2$, or $-\text{Si}(\text{R}^5)_2\text{N}(\text{R}^5)-$ groups, wherein R^5 is a C_{1-20} aliphatic or cycloaliphatic group, and R^6 is R^5 or a C_{6-20} aryl group or sulfonate ester such as tosyl or mesyl. Most preferably, Lg is halo, especially bromo.

- 10 When further cyclopentadienyl substituted compounds are desired, the final elimination step may be followed by further substitution of Lg with a functional substituent or even formation of dimeric bridged ligands through a coupling of ligand groups, utilizing techniques well known to the skilled artisan. Highly preferred functional substituents include metals, hydrocarbyl, silyl, hydrocarbyl- or polyhydrocarbyl- substituted silyl, silyl- or polysilyl- substituted hydrocarbyl groups,
- 15 metallated derivatives of such hydrocarbyl, silyl, substituted silyl or substituted hydrocarbyl groups, or bridging groups of the formula: $-\text{Z}'\text{Y}-$ when a coupled product is formed, or masked, metallated, or coupled derivatives thereof, said functional substituent having up to 50 atoms not counting hydrogen, wherein:

Y is $-\text{O}-$, $-\text{S}-$, $-\text{NR}^5-$, $-\text{PR}^5-$, $-\text{NR}^5_2$, $-\text{PR}^5_2$, or

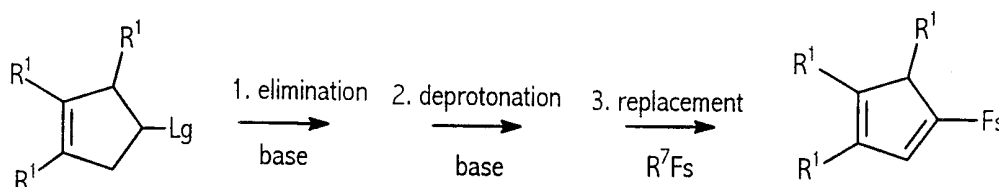


- 20 Z' is SiR^5_2 , CR^5_2 , $\text{SiR}^5_2\text{SiR}^5_2$, $\text{CR}^5_2\text{CR}^5_2$, $\text{CR}^5=\text{CR}^5$, $\text{CR}^5_2\text{SiR}^5_2$, BR^5 , $\text{B}=\text{NR}^5_2$, or GeR^5_2 ; and

- R^5 each occurrence is independently hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R^5 having up to 20 non-hydrogen atoms, and optionally,
- 25 two R^5 groups from Z' (when R^5 is not hydrogen), or an R^5 group from Z' and an R^5 group from Y form a ring system.

Masked derivatives of the foregoing ligands are those ligands containing an easily removable group at the position desired for later coupling or further

functionalization of the compound. An example is a trihydrocarbylsilyl group, especially trimethylsilyl. In a highly preferred embodiment of the invention the foregoing Lg group is replaced with the desired functional ligand group in a single step which is a combination of elimination, deprotonation and replacement operations using two equivalents of base for each equivalent of cyclopentadiene compound and the addition of the source for the functional group, R^7Fs , where R^7 is a leaving group, preferably halogen or a sulfonate ester, and Fs is a functional substituent, preferably $Z'YH$. Because the combination of three processes in one step does not involve dehydration of an alcohol intermediate, formation of dimeric byproducts through a Diels-Alder reaction of the diene is avoided. This combined process may be illustrated schematically as follows:



Finally according to the present invention there is provided a process for preparing metal complexes comprising cyclopentadienyl- or substituted cyclopentadienyl- ligands using one or all of the foregoing intermediate process steps. The present processes result in the highly efficient production of metal complexes and metal complex intermediates.

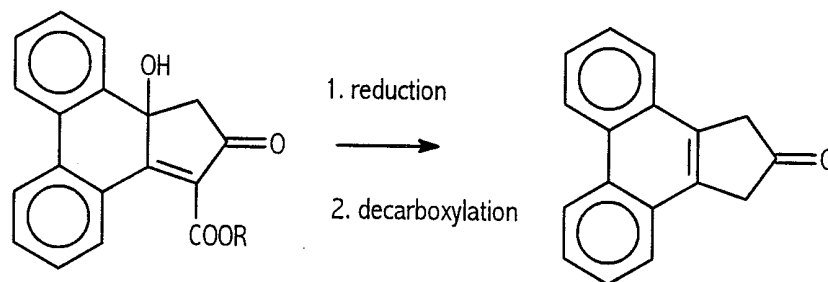
All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1995. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. The term "hydrocarbyl" where used generically includes alkyl, aryl, cycloalkyl, aralkyl and alkaryl groups.

The hydrolysis and condensation reactions are suitably performed in a diluent comprising a mixture of one or more organic acids and one or more inorganic halides at a temperature from 0 to 200°C, preferably 50-150 °C. A preferred organic acid is acetic acid. A preferred acid mixture is a combination of glacial acetic acid and concentrated hydrochloric acid, most preferably in a volume of 10/1 to 1/1. Preferably the metal is finely comminuted, uniformly dispersed in the acid mixture, and used in approximately an equimolar ratio with the ketoester. The ketone product is suitably recovered by adding the mixture to water, cooling and recovering the product by separation from the

aqueous mixture.

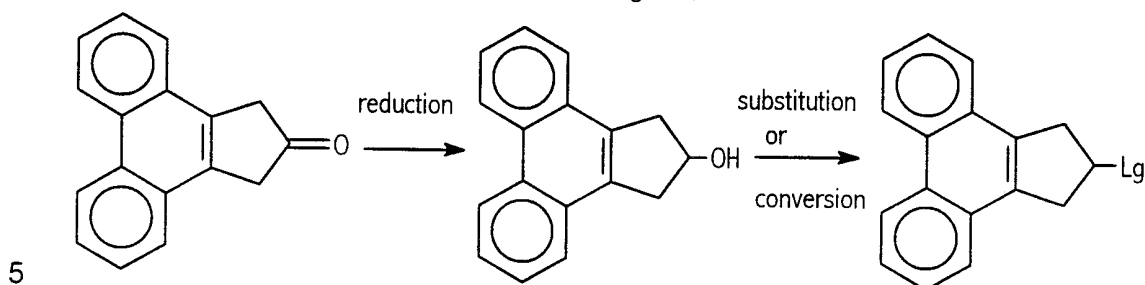
The reduction of the ketone can be accomplished using sodium borohydride or similar reducing agent in a solvent or diluent at a temperature from 0 to 150 °C., followed by quenching with an acid. A suitable diluent
5 mixture is a chloroform/ethanol mixture, preferably in a volume ratio from 10/50 to 90/10, most preferably about 50/10. The final steps of substitution and elimination may be conducted at temperatures from 0 to 150 °C using multiple steps or combining the separate steps. The initial substitution is desirable conducted in the presence of an acid acceptor such as pyridine.
10 Highly desirably, the hydroxyl group is first converted to a sulfonic acid ester by reaction with, methanesulfonyl chloride which is readily converted to the halide by reaction with a metal halide such as lithium bromide. The foregoing steps are desirably conducted in the presence of an organic solvent, such as methylenechloride for the first step and acetone for the second step. The final
15 step in formation of the cyclopentadiene or cyclopentadienyl ligand uses standard organometallic techniques, generally metalization or similar metathesis reactions depending on the desired final product. The skilled artisan will appreciate that the final step of elimination (or deprotonation) may be combined with a functionalizing step if desired. When the preferred
20 combination of elimination/ deprotonation, and replacement operations are performed in one step, two or more equivalents of a base, preferably from 2 to 2.5 equivalents, are used to cause both elimination and deprotonation, and the functionalizing reagent, R⁷Fs is added after the deprotonation step is completed or substantially completed. A preferred functionalizing reagent is
25 R⁷-Z⁷Y-H.

The present process has proven to be highly desirable in the formation of certain bulky multiring cyclopentadiene derivatives, specifically 1H-cyclopenta(*f*)phenanthrene derivatives. Especially desirable is its use in a process for forming 2,3-dihydro-2-oxo-1H-cyclopenta(*f*)phenanthrene by reaction of an alkyl 3,3a-dihydro-3a-hydroxy-2-oxo-2H-cyclopenta(*f*)phenanthrene-1-carboxylate. This may be
30 illustrated schematically as follows:



wherein R is as previously defined.

In the subsequent steps, the ketone is converted to a 2,3-dihydro-2-substituted-(1H)cyclopenta(1)phenanthrene ligand, as follows:



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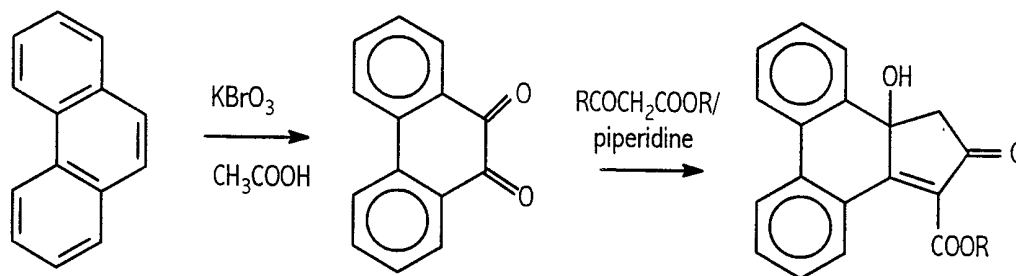
wherein Lg is as previously defined.

In the final steps, the 2,3-dihydro-2'-substituted-1H-cyclopenta(1)phenanthrene compound may be converted to the desired ligand group for further synthesis using standard metalizing and substitution procedures.

10

Alkyl 3,3a-dihydro-3a-hydroxy-2-oxo-2H-cyclopenta(1)phenanthrene-1-carboxylate compounds for use in the foregoing procedure are prepared according to known techniques. One suitable technique is condensation of 9,10-phenanthrene quinone with an alkyl acetoacetate, such as methyl acetoacetate or ethyl acetoacetate, in the presence of an acid acceptor such as piperidine. The initial 9,10-phenanthrene quinone, if not available commercially, may be readily prepared by reaction of phenanthrene with excess acetic acid in the presence of an oxidizing agent such as potassium bromate. The foregoing synthetic procedures are illustrated as follows:

15



20

wherein R is as previously defined.

As previously mentioned, the foregoing syntheses are useful in preparing ligands for metal complexes that are components of addition polymerization catalyst compositions. Preferred metal complexes generally correspond to the formula: $CpZMX_xL_lX'_x$ (IA);

5 where Cp is a cyclopentadienyl ligand derived from the foregoing cyclopentadienyl or substituted cyclopentadienyl compounds;

M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

Z is either a cyclic or noncyclic ligand group containing delocalized π -electrons, including a second cyclopentadienyl ring system group as herein previously disclosed for Cp, said Z being bonded to M by means of delocalized π -electrons and optionally covalently bonded to Cp through a divalent bridging group, or Z is a divalent moiety lacking in delocalized π -electrons that is covalently bonded to Cp and M, or such a moiety comprising one σ -bond by which it is bonded to Cp, and a neutral two electron pair able to form a coordinate-covalent bond to M, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

15 X is a monovalent anionic ligand group having up to 60 atoms other than hydrogen;

L independently each occurrence is a neutral ligand having up to 20 atoms;

20 X' is a divalent anionic ligand group having up to 60 atoms;

x is 0, 1, 2, or 3;

l is a number from 0 to 2, and

x' is 0 or 1.

The above complexes may exist as isolated crystals optionally in pure form, or as a mixture with other complexes, in the form of a solvated adduct, optionally in a solvent, especially an organic liquid, as well as in the form of a dimer or chelated derivative thereof, wherein the chelating agent is an organic material such as ethylenediaminetetraacetic acid (EDTA).

The catalyst compositions for olefin polymerization generally comprise:

- 30 A. 1) a metal complex of formula (IA), and
2) an activating cocatalyst,

the molar ratio of 1) to 2) being from 1:10,000 to 100:1, or

B. the reaction product formed by converting a metal complex of formula (IA) to an active catalyst by use of an activating technique.

The olefin polymerization processes generally comprise contacting one or more C₂₋₂₀ α-olefins under polymerization conditions with a catalyst comprising:

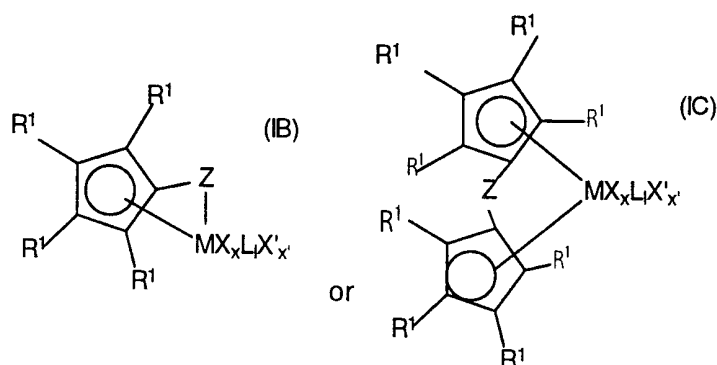
- A. 1) a metal complex of formula (IA), and
2) an activating cocatalyst,

5 the molar ratio of 1) to 2) being from 1:10,000 to 100:1, or

- B. the reaction product formed by converting a metal complex of formula (IA) to an active catalyst by use of an activating technique.

The catalyst compositions may also be supported on a support material and used in olefin polymerization processes in a slurry or in the gas phase. The catalyst
10 may be prepolymerized with one or more olefin monomers *in situ* in a polymerization reactor or in a separate process with intermediate recovery of the prepolymerized catalyst prior to the primary polymerization process.

Highly preferred metal complexes prepared by using the cyclopentadiene compounds prepared by the present process correspond to
15 the formula:



where M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

R¹ independently each occurrence is hydrogen, hydrocarbyl, silyl, germyl,
20 halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo- substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, silyl- substituted hydrocarbyl, hydrocarbylsiloxy- substituted hydrocarbyl, hydrocarbylsilylamino- substituted
25 hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino- substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said R¹ group having up to 40 atoms not counting hydrogen atoms, and

optionally two or more of the foregoing adjacent R¹ groups may together form a divalent derivative thereby forming a saturated or unsaturated fused ring, and further optionally one or more of the carbons of any of the rings may be replaced by a nitrogen or sulfur atom;

5 Z is a divalent moiety lacking in delocalized π -electrons, or such a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

10 X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic ligand groups bound to M through delocalized π -electrons;

 L independently each occurrence is a neutral ligating compound having up to 20 atoms;

15 X' is a divalent anionic ligand group having up to 60 atoms;

 x is 0, 1, 2, or 3;

 l is a number from 0 to 2, and

 x' is 0 or 1.

 In the metal complexes, preferred L groups are carbon monoxide; phosphines, especially trimethylphosphine, triethylphosphine, triphenylphosphine and bis(1,2-dimethylphosphino)ethane; P(OR⁴)₃, wherein R⁴ is C₁₋₂₀ hydrocarbyl; ethers, especially tetrahydrofuran; amines, especially pyridine, bipyridine, tetramethylethylenediamine (TMEDA), and triethylamine; olefins; and neutral conjugated dienes having from 4 to 40, preferably 5 to 40 carbon atoms. Complexes including such neutral diene L groups are those wherein the metal is in the +2 formal oxidation state.

 Further in reference to the metal complexes, X preferably is selected from the group consisting of hydro, halo, hydrocarbyl, silyl, and N,N-dialkylamino-substituted hydrocarbyl. The number of X groups depends on the oxidation state of M, whether Z is divalent or not and whether any neutral diene groups or divalent X' groups are present. The skilled artisan will appreciate that the quantity of the various substituents and the identity of Z are chosen to provide charge balance, thereby resulting in a neutral metal complex. For example, when Z is divalent, and x is zero, x' is two less than the formal oxidation state of M. When Z contains one neutral two electron coordinate-covalent bonding site, and M is in a formal oxidation state of +3, x

may equal zero and x' equal 1, or x may equal 2 and x' equal zero. In a final example, if M is in a formal oxidation state of +2, Z may be a divalent ligand group, whereupon x and x' are both equal to zero and one neutral L ligand group may be present.

5 The complexes can be prepared by combining a Group 4 metal tetrahalide or tetraamide salt with the corresponding cyclopentadienyl ring system ligand dianion in an inert diluent. Optionally a reducing agent can be employed to produce the lower oxidation state complexes, and standard ligand exchange procedures can be used to produce different ligand substituents.

10 Processes that are suitably adapted for use herein are well known to synthetic organometallic chemists. The synthesis of the cyclopentadiene compounds, derivatives thereof, and metal complexes, and all other preparations herein, unless stated to the contrary, are conducted in a suitable noninterfering solvent at a temperature from -100 to 300°C, preferably from -80 to 150°C, most preferably from 0
15 to 50°C. By the term "reducing agent" herein is meant a metal or compound which, under reducing conditions causes the metal M , to be reduced from a higher to a lower oxidation state, or for organic syntheses, causes addition of hydrogen to the compound. Examples of suitable metal reducing agents are alkali metals, alkaline earth metals, aluminum and zinc, alloys of alkali metals or alkaline earth metals such
20 as sodium/mercury amalgam and sodium/potassium alloy. Examples of suitable reducing agent compounds are sodium naphthalenide, potassium graphite, lithium alkyls, lithium or potassium alkadienyls; and Grignard reagents. Most preferred reducing agents are the alkali metals or alkaline earth metals, especially lithium and magnesium metal. By the term "oxidizing agent" herein is meant a metal or
25 compound which causes the metal M , to be oxidized from a lower to a higher oxidation state, or for organic syntheses, causes addition of oxygen to the compound. Suitable oxidizing agents for organometallic oxidations include chlorinated hydrocarbons, especially methylenechloride. Suitable oxidizing agents for organic
syntheses include potassium bromate.

30 Suitable reaction media for the formation of the complexes include aliphatic and aromatic hydrocarbons, ethers, and cyclic ethers, particularly branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane,
cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof;
35 aromatic and hydrocarbyl-substituted aromatic compounds such as benzene, toluene, and xylene, C_{1-4} dialkyl ethers, C_{1-4} dialkyl ether derivatives of (poly)alkylene glycols,

and tetrahydrofuran. Mixtures of the foregoing are also suitable. All of the foregoing steps are conducted according to well known organic or organometallic synthetic techniques.

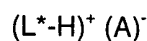
5 The complexes are rendered catalytically active by combination with an activating cocatalyst or by use of an activating technique. Suitable activating
cocatalysts for use herein include polymeric or oligomeric alumoxanes, especially
methylalumoxane, triisobutyl aluminum modified methylalumoxane, or
isobutylalumoxane; neutral Lewis acids, such as C₁₋₃₀ hydrocarbyl substituted Group
10 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron
compounds and halogenated (including perhalogenated) derivatives thereof, having
from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more
especially perfluorinated tri(aryl)boron compounds, and most especially
tris(pentafluorophenyl)borane; nonpolymeric, compatible, noncoordinating, ion
15 forming compounds (including the use of such compounds under oxidizing
conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-,
silylium- or sulfonium- salts of compatible, noncoordinating anions, or ferrocenium
salts of compatible, noncoordinating anions; bulk electrolysis (explained in more detail
hereinafter); and combinations of the foregoing activating cocatalysts and techniques.
The foregoing activating cocatalysts and activating techniques have been previously
20 taught with respect to different metal complexes in the following references:
US-A-5,153,157, US-A-5,064,802, US-A-5,321,106, US-A-5,350,723, and
EP-A-520,732. Combinations of neutral Lewis acids, especially the combination of a
trialkyl aluminum compound having from 1 to 4 carbons in each alkyl group and a
halogenated tri(hydrocarbyl)boron compound having from 1 to 20 carbons in each
25 hydrocarbyl group, especially tris(pentafluorophenyl)borane, further combinations of
such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and
combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane
with a polymeric or oligomeric alumoxane are especially desirable activating
cocatalysts. Preferred molar ratios of Group 4 metal complex:tris(pentafluorophenyl-
30 borane:alumoxane are from 1:1:1 to 1:5:20, more preferably from 1:1:1.5 to 1:5:10.

Suitable ion forming compounds useful as cocatalysts in one embodiment of
the present invention comprise a cation which is a Bronsted acid capable of donating
a proton, and a compatible, noncoordinating anion, A⁻. As used herein, the term
"noncoordinating" means an anion or substance which either does not coordinate to
35 the Group 4 metal containing precursor complex and the catalytic derivative derived
therefrom, or which is only weakly coordinated to such complexes thereby remaining

sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating anion specifically refers to an anion which when functioning as a charge balancing anion in a cationic metal complex does not transfer an anionic substituent or fragment thereof to said cation thereby forming neutral complexes. "Compatible anions" are anions
 5 which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of
 10 balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids
 15 include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

Preferably such cocatalysts may be represented by the following general
 20 formula:



wherein:

L* is a neutral Lewis base;

(L*-H)⁺ is a conjugate Bronsted acid of L*^{*}; and

25 A⁻ is a noncoordinating, compatible anion having a charge of -1.

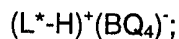
More preferably A⁻ corresponds to the formula: [M'Q₄]⁻;

wherein:

M' is boron or aluminum in the +3 formal oxidation state; and

30 Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxy Q
 35 groups are disclosed in U. S. Patent 5,296,433.

Activating cocatalysts comprising boron which are particularly useful in the preparation of catalyst compositions may be represented by the following general formula:



5 wherein:

L* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen
10 atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

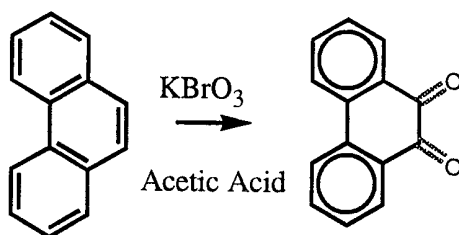
Preferred Lewis base salts are ammonium salts, more preferably trialkylammonium salts containing one or more C₁₂₋₄₀ alkyl groups, most preferably methyldioctadecylammonium or dimethyloctadecylammonium salts. Most preferably, Q is each occurrence an inertly substituted aryl group, especially, a pentafluorophenyl
15 or p-dialkylaluminoxyphenyl.

Examples

The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed. The following examples are provided as further illustration of the invention and are not
20 to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis. All syntheses of air or water sensitive compounds were performed under dry nitrogen or argon atmosphere using a combination of glove box and high vacuum techniques. Solvents were purified by passing through double columns charged with activated alumina and a purification catalyst (Q-5[®] catalyst
25 available from Englehardt Corporation). The term "overnight", if used, refers to a time of approximately 16-18 hours, "room temperature", if used, refers to a temperature of about 20-25 °C, and "mixed alkanes" refers to a mixture of mostly C₆-C₁₂ alkanes available commercially under the trademark Isopar E[™] from Exxon Chemicals Inc.

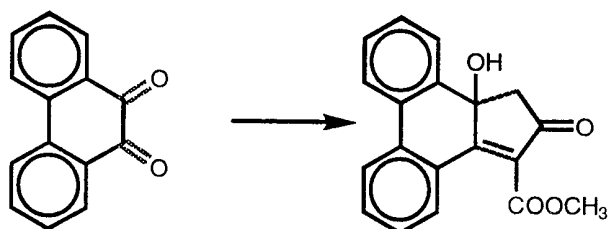
Example 1 Synthesis of 2,3-dihydro-2-oxo-1H-
30 cyclopenta(1)phenanthrene

(1) Preparation of Phenanthrenequinone:



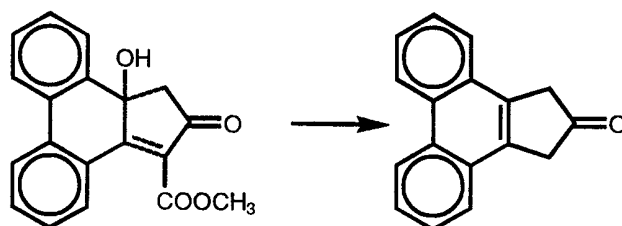
Phenanthrene (16g , Aldrich Tech Grade (90 percent), 0.081 mol) and acetic acid (200ml) were stirred and heated to 70-75 °C. Potassium bromate (32g, 0.19 mol) was added in 2 portions. After the addition of the first portion the temperature rose to reflux with evolution of bromine vapors. The second portion was added and the condenser was replaced by a distillation head. The heating was continued until the distillate was colorless. The deep red solution was cooled and poured into water (300ml) and the precipitate was isolated by filtration. The crude product was purified by reslurrying in 100ml of hot (70 °C) aqueous sodium bisulfite solution (40 percent) and filtering while hot. The deep red filtrate was cooled and treated with aqueous sodium carbonate until basic. The precipitated product was recovered by extraction with methylene chloride, dried and concentrated to yield 13.4g (80 percent yield) of orange yellow solid : mp 182-184 °C.

(2) Preparation of 2,11b-dihydro-11b-hydroxy-2-oxo-1H-cyclopenta[1]phenanthrene-3-carboxylic acid methyl ester.



A slurry of phenanthrenequinone (10.5g, 0.05 mol) in ethanol (60ml) containing methyl acetoacetate (6.96g, 0.06 mol) and piperidine (6-8 drops) was refluxed for 2 to 2.5 h. The quinone eventually dissolved and the entire reaction mixture solidified. Filtration of the cooled mixture gave 14.3g (93 percent) of a white solid: ¹H NMR (CDCl₃, δ) 3.21(d of d, 2H, J=18Hz), 3.87(s, 3H), 7.3-8.0(m, 8H).

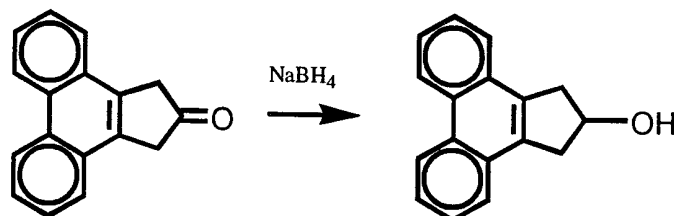
(3) Preparation of 1,3-Dihydro-2H-Cyclopenta[1]phenanthrene-2-one



The ketoester of step 2 (14.1g, 0.046mol) was added to a mixture of acetic acid (150ml) and hydrochloric acid (5ml) containing zinc dust (6g, 0.092 mol). The mixture immediately solidified. The mixture was slowly heated to reflux when all the solids dissolved giving a clear yellow solution containing unreacted zinc granules.

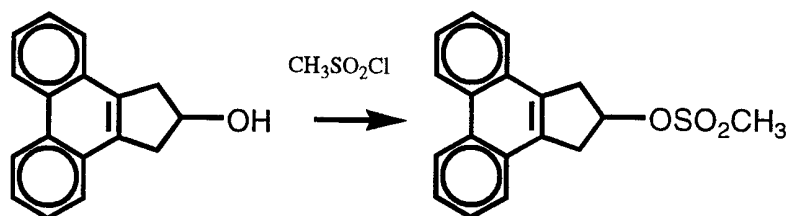
- 5 The mixture was refluxed for 4 h and filtered while hot. The filtrate was cooled and poured into ice water. The resulting white precipitate was filtered and dried. A small amount of the product that had crystallized out during the hot filtration was recovered by extraction with methylene chloride and concentrating to yield the product. The combined yield was 10.4g (97.3 percent). ¹H NMR (CDCl₃, δ) 3.71(s, 4H), 7.62(bs, 6H), 8.68(d, 2H, J=7Hz).
- 10

(4) Preparation of 2,3-Dihydro-1H-Cyclopenta[*l*]phenanthrene-2-ol



- Sodium borohydride (1g, 0.027 mol) was added to a slurry of 2,3-Dihydro-2H-Cyclopenta[*l*]phenanthrene-2-one (4.6g, 0.02 mol) in 50ml of chloroform and 10 ml of ethanol. The resulting yellow solution was stirred overnight and quenched with 10 percent aqueous HCl. The mixture was transferred to a separatory funnel and the organic layer was washed with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate and concentrated under reduced pressure to yield the product as a yellowish white solid. Yield was 4.7g, 100 percent). ¹H NMR (CDCl₃-
- 15
- 20 DMSO -d₆, δ) 3.31 (d, 2H, J=16 Hz), 3.56 (d of d, 2H, J=16, 6 Hz), 4.76 (brs, 1H), 4.91 (brs, 1H), 7.59-7.85 (m, 6H), 8.67-8.70 (m, 2H).

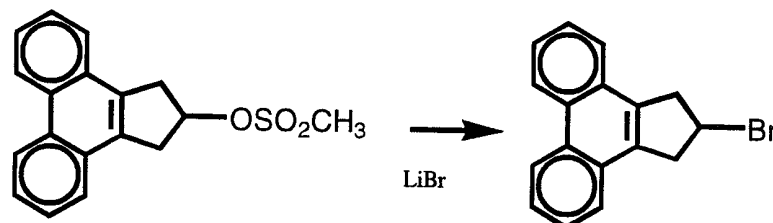
(5) Preparation of 2,3-Dihydro-1H-Cyclopenta[*l*]phenanthrene-2-ol methanesulfonate



- 25 To a stirred suspension of 2,3-dihydro-1H-cyclopentaphenanthrene-2-ol (2.34g, 0.01 mol) in 20 ml of pyridine was added a solution of methanesulfonyl chloride (2.28g, 0.02 mol) in 15 ml of methylene chloride and allowed to stir for 2hr at room temperature. The reaction mixture was worked up by washing with 10

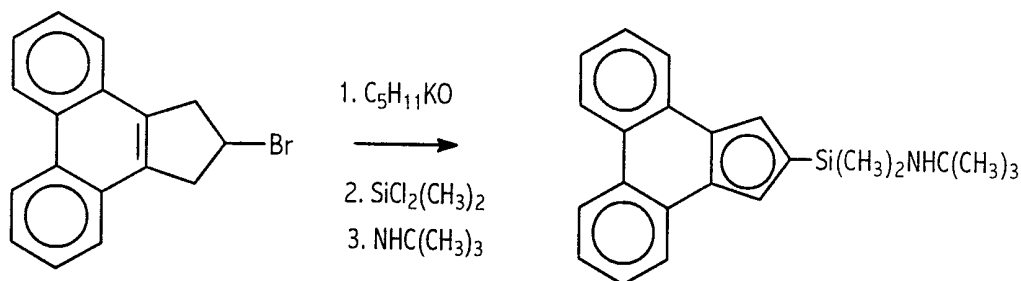
percent aqueous HCl, drying over anhydrous magnesium sulfate and concentrating under reduced pressure to yield the methanesulfonate as a tan solid (3.11g, 100 percent). ^1H NMR (CDCl_3 , δ) 3.05 (s, 3H), 3.58-3.69 (m, 4H), 5.75 (m, 1H), 7.60-7.76 (m, 6H), 8.68 (m, 2H).

5 (6) Preparation of 2-Bromo-2,3-Dihydro-1H-Cyclopenta[*b*]phenanthrene



A mixture of 2,3-Dihydro-1H-Cyclopenta[*b*]phenanthrene-2-ol methanesulfonate (3.11g, 0.01 mol) and lithium bromide (2.61g, 0.03 mol) in 50 ml of acetone was refluxed for 18 hr. The reaction mixture was worked up by concentrating to remove the volatiles and extracting with a mixture of methylene chloride and hexane(1:3) and filtering through silica gel to yield 2.34g (80 percent) of the bromide as a buff colored solid. ^1H NMR (CDCl_3 , δ) 3.73-3.94 (m, 4H), 4.97 (m, 1H), 7.58-7.76 (m, 6H), 8.66 (m, 2H); ^{13}C NMR (CDCl_3 , δ) 44.34, 47.28, 123.20, 124.69, 126.07, 126.83, 129.17, 130.38, 134.40.

15 (7) Preparation of (1H-Cyclopenta[*b*]phenanthrene-2-yl)dimethyl(*t*-butylamino)silane

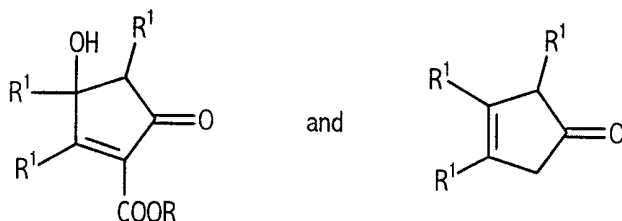


To a solution of 2-bromo-cyclopentaphenanthrene (0.500 g, 1.68 mmol) in 40 mL THF was added 25 percent (wt/wt) potassium amylate in cyclohexane (2.0g, 3.7 mmol). The solution color changed to orange immediately and a precipitate formed. The mixture was heated to reflux. After 30 minutes heating the mixture was cooled and the volatile materials were removed under reduced pressure. The residue was slurried in 30 mL THF and this mixture was added slowly to neat dichlorodimethylsilane (2.0 mL, 17 mmol). The resulting mixture was pale yellow. Fifteen minutes after the addition was complete, volatile materials were removed under reduced pressure. The residue was slurried in 30 mL THF and *tert*-butylamine was added to the resulting mixture which was left to stir overnight. The volatile

materials were removed under reduced pressure and the resulting residue was extracted three times with a total of 60 mL of mixed hexanes. The extracts were filtered and volatile materials were removed from the combined filtrates under reduced pressure. The product was formed as white crystals upon cooling. Yield of
5 the desired product was 0.575 g, 99 percent.

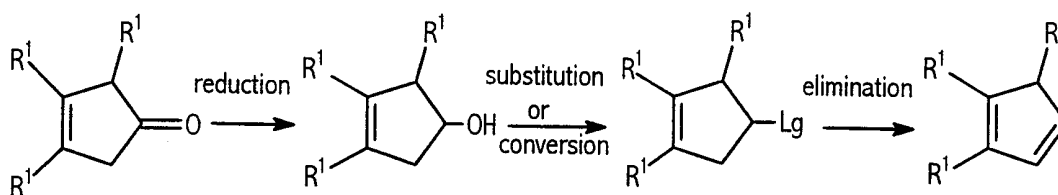
CLAIMS:

1. A process for forming a 4-ketocyclopentene compound comprising reducing a 1-carbohydrocarbyloxy-2-keto-4-hydroxy-5-cyclopentene compound by contacting with a metal and decarboxylating the resulting reaction product.
- 5 2. The process of claim 1 wherein the decarboxylation is conducted by contacting the reaction product with a mixture of an organic acid and an inorganic chloride compound.
3. The process of claim 1 wherein the metal is zinc, the organic acid is acetic acid, the inorganic chloride compound is hydrochloric acid, and the 1-
- 10 carbohydrocarbyloxy-2-keto-4-hydroxy-5-cyclopentene and 4-ketocyclopentene compounds correspond to the formula:



- wherein, R is C₁₋₂₀ hydrocarbyl, preferably C₁₋₄ alkyl; and
- R¹ independently each occurrence is hydrogen, hydrocarbyl, silyl, germyl,
- 15 halide, or halo- substituted hydrocarbyl, said R¹ group having up to 40 atoms not counting hydrogen atoms, and optionally two or more of the foregoing adjacent R¹ groups may together form a divalent derivative thereby forming a saturated or
- unsaturated fused ring or multiple ring system, and further optionally one or more of
- the carbons of R¹ in any of the so formed rings may be replaced by a nitrogen, boron,
- 20 phosphorus or sulfur atom.

4. The process of claim 1 wherein 2,3-dihydro-2-oxo-1H-cyclopenta(l)phenanthrene is prepared from a C₁₋₂₀ alkyl 3,3a-dihydro-3a-hydroxy-2-oxo-2H-cyclopenta(l)phenanthrene-1-carboxylate.
5. A process for preparing a cyclopentadiene or substituted
- 25 cyclopentadiene compound, the steps of the process comprising reducing a ketone to form an alcohol, replacing the hydroxyl functionality of the alcohol under substitution conditions with a leaving group, and deprotonating the resulting product under base induced elimination conditions to form the cyclopentadiene compound, wherein the ketone, alcohol, substituted product and cyclopentadiene correspond to the following
- 30 formulas, and the process corresponds to the following scheme:

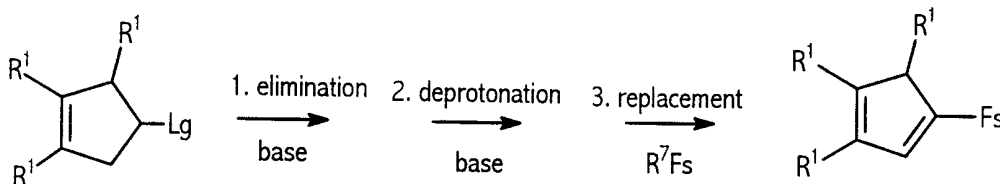


wherein R^1 is as previously defined in claim 3, and

Lg is a suitable ligand group that is subject to base induced elimination.

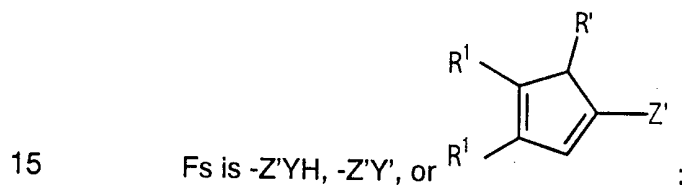
5 6. The process of claim 5 wherein the ketone is prepared according to the process of claim 3.

7. A process for preparing a functionalized cyclopentadienyl compound by reacting a substituted cyclopentene compound with at least two equivalents of a base and a source of the functionalizing ligand, said process comprising in
10 combination an elimination, deprotonation and replacement operation illustrated schematically as follows:



wherein, Lg is as defined in claim 5;

R^7 is a leaving group, and



wherein Y is $-O-$, $-S-$, $-NR^5$, or $-PR^5$,

Y' is $-NR^5_2$, or $-PR^5_2$;

Z' is SiR^5_2 , CR^5_2 , $SiR^5_2SiR^5_2$, $CR^5_2CR^5_2$, $CR^5=CR^5$, $CR^5_2SiR^5_2$, BR^5 , $B=NR^5_2$, or GeR^5_2 ; and

20 R^5 each occurrence is independently hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R^5 having up to 20 non-hydrogen atoms, and optionally, two R^5 groups from Z' (when R^5 is not hydrogen), or an R^5 group from Z' and an R^5 group from Y form a ring system.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/27395

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C45/67 C07C49/665 C07C13/66 C07F7/10

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C07F

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>COPE ARTHUR C ET AL: "The condensation product of 9,10-phenanthrenequinone and ethyl acetoacetate" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol. 80, 1958, pages 5513-5516, XP002130061 AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC., US ISSN: 0002-7863 page 5514 -page 5515</p> <p style="text-align: center;">— — — — — -/-</p>	1-7

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

9 February 2000

Date of mailing of the international search report

28/02/2000

Name and mailing address of the ISA

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 NL - 2280 HV Rijswijk
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Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Internat J Application No

PCT/US 99/27395

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	COPE ARTHUR C ET AL: "The rearrangement of allyl groups in three-carbon systems. VI. Benzene and phenanthrene derivatives" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol. 78, 1956, pages 2547-2551, XP002130062 AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC., US ISSN: 0002-7863 pages 2548, 2550, 2551	1-7
Y	COOPER R M ET AL: "Acetolysis of 2-(2,3-dihydro-1H-cyclopenta[1]phenanthren-2-yl)ethyl derivatives: participation by the 9,10-bond of phenanthrene to give an analog of a classical norbornyl cation" J. CHEM. SOC., PERKIN TRANS. 2 (JCPKBH);1972; (5); PP.594-8, XP002130063 King's Coll.;Dep. Chem.; London; Engl. page 596, column 2 -page 597, column 1	1-7
Y	US 2 656 390 A (STOLL MAX) 20 October 1953 (1953-10-20) claims	1-7
P,A	WO 99 14221 A (DOW CHEMICAL CO) 25 March 1999 (1999-03-25) example 1	7
P,A	WO 99 40096 A (BOULDER SCIENT CO) 12 August 1999 (1999-08-12) page 2; claims	7

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat	Application No
PCT/US 99/27395	

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
US 2656390	A	20-10-1953	DE 862891 C FR 969480 A GB 663183 A NL 68849 C	20-12-1950
WO 9914221	A	25-03-1999	AU 8699798 A	05-04-1999
WO 9940096	A	12-08-1999	US 5965757 A AU 2491899 A	12-10-1999 23-08-1999