



(51) International Patent Classification:
C07C 23/38 (2006.01)

(21) International Application Number:
PCT/EP2017/077548

(22) International Filing Date:
27 October 2017 (27.10.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201641037033 28 October 2016 (28.10.2016) IN

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR PREPARATION OF SUBSTITUTED 2-HALO-BENZINDENE COMPOUNDS

(57) Abstract: The invention relates to a process for the preparation of substituted 2-halo-benzindene compounds. The invention further relates to a process for the preparation of a metallocene complex from such substituted 2-halo-benzindene compounds. The invention further relates to a process for the preparation of a catalyst for a solution polymerization of olefin from such substituted 2-halo-benzindene compounds.



PROCESS FOR PREPARATION OF SUBSTITUTED 2-HALO-BENZINDENE
COMPOUNDS

5 The invention relates to a process for the preparation of substituted 2-halo-benzindene compounds. The invention further relates to a process for the preparation of a metallocene complex from such substituted 2-halo-benzindene compounds. The invention further relates to a process for the preparation of a catalyst for a solution polymerization of olefin from such substituted 2-halo-benzindene compounds.

10 Substituted 2-halo-benzindene compounds are commercially very attractive and can be used for preparation of metallocene complexes and can be further used as a catalyst for olefin polymerization.

15 Metallocene complexes with bridged benzindenyl ligands have proven to be highly active in the polymerization of α -olefins such as ethylene after activation with aluminoxane co-catalysts. However, known processes for the preparation of 2-halo-benzindene compounds require many steps and are tedious.

20 For instance, Ijpeij, E et al. describes in the Journal of Organic Chemistry, 2002, Vol. 67, pages 169-176, a process for preparation of 2-bromo-benzindene compound of formula (5), wherein (wherein R1, R2, R3, R4, R7 and R8 all stand for H) following procedure by Spaleck, W. et al. in the Organometallics 1994, 13, 954. However this particular process requires 9 steps process for preparation 2-2-bromo-benzindene compound, considering the preparation from 2-methyl naphthalene. Also the process requires harsh reaction
25 conditions such as a temperature of 180 °C for the decarboxylation step and is therefore also difficult to scale-up.

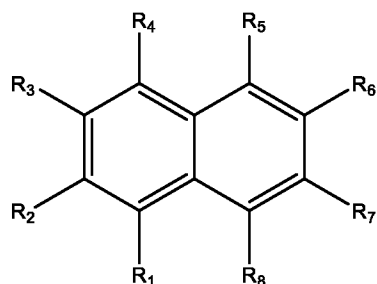
Rendina, V. et al. also disclosed a similar process in Tetrahedron Letters, 2012, Vol. 53
30 pages 15–18 for the preparation of bromohydrin compound, which required 8 steps.

These processes rely on 8 to 9 step process for the preparation of 2-bromo-benzindene compound considering the preparation from 2-methyl naphthalene. Also these processes suffer from lower yields and harsh reaction conditions.

Therefore it is an objective of the present invention to provide an economically feasible simpler process for the preparation of substituted 2-halo-benzindene compounds.

Accordingly, the invention provides a process for the preparation of a substituted 2-halo-benzindene compound, comprising the steps of:

5 a) Friedel Crafts acylation of an aromatic compound of formula (1) with 3-chloropropionyl chloride in the presence of a Lewis acid to form a corresponding acylated compound,

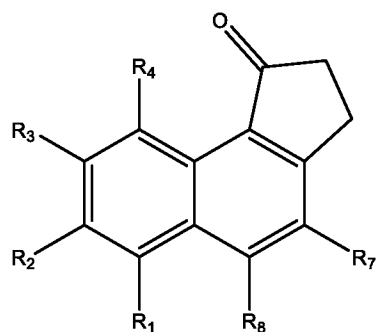


formula (1)

wherein R1, R2, R3, R4, R5, R6, R7, R8 each independently stands for H, a hydrocarbon radical having 1-20 carbon atoms, a halide, an alkoxy having 1-6 C atoms, an alkyl sulphide, an amine, a Si or B-containing group or a P-containing group;

10

b) cyclization of the acylated compound with a mineral acid to form a corresponding substituted benzinda-1-one compound of formula (2),

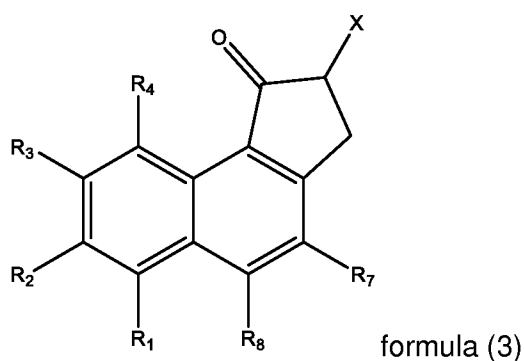


formula (2)

15

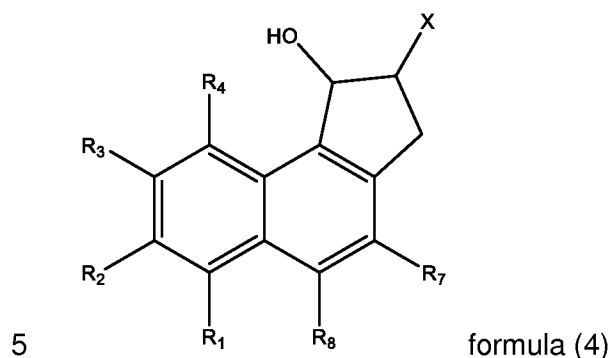
wherein R1, R2, R3, R4, R7, R8 are as described for formula (1);

c) halogenation of compound of formula (2) with a halogenating agent to form a corresponding substituted 2-halo-benzinda-1-one compound of formula (3),



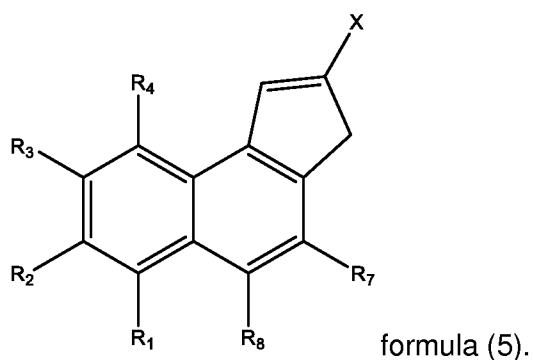
wherein R1, R2, R3, R4, R7, R8 are as described for formula (1) and X is halogen;

d) reduction of compound of formula (3) with a reducing agent to form a corresponding substituted 2-halo-benzinda-1-ol of formula (4),



wherein R1, R2, R3, R4, R7, R8 are as described for formula (1) and X is halogen;

e) dehydration of compound of formula (4) with a dehydration agent to obtain the substituted 2-halo-benzindene compound of formula (5),



According to the process of the invention, the substituted 2-halo-benzindene compound of formula (5) is obtained by a simple process with fewer steps than by the processes of the prior art. The yield of the process according to the invention is relatively high and the reaction conditions are relatively mild. Compounds of formula (5) can be used for the preparation of metallocene complexes.

15

Preferably, R1, R2, R3, R4, R5, R6, R7, R8 each stands for H.

Preferably, X stands for Br.

5

Step a)

In step a), an aromatic compound of formula (1) is reacted with 3-chloropropionyl chloride in the presence of a Lewis acid at a reaction temperature to form a corresponding acylated compound by Friedel Crafts acylation.

10

The Lewis acid may e.g. be a metal halide or a non-metal halide. The metal halide may for example be aluminium chloride or ferric chloride. The non-metal halide may for example be boron trifluoride or boron trifluoride diethyl etherate;

15

Other examples of the Lewis acid include tungstophosphate, for example aluminum dodecatungstophosphate; clay for example montmorillonite; sulphonic acid for example trifluoromethanesulfonic acid.

20

The Friedel Crafts acylation of step a) may in principle be performed in any solvent known to be suitable for Friedel Crafts acylation. Examples of suitable solvents include halogenated solvents, for example 1,2-dichloroethane (= ethylene dichloride), 1,2-dichloromethane, chloroform, carbon tetrachloride; disulphide for example carbon disulphide; and combinations thereof. Particularly preferred is 1,2-dichloroethane.

25

Step a) may be performed by an addition of the compound of formula (1) to the other components or vice versa, followed by stirring at a reaction temperature. Preferably, step a) is performed by adding a solution of the aromatic compound of formula (1) in a solvent to a solution of 3-chloropropionyl chloride and the Lewis acid in a solvent and stirring at a reaction temperature. The temperature, pressures and reaction time known to be suitable for Friedel Crafts acylation by the person skilled in the art may be used. Optimal conditions can be found using routine experimentation. The obtained mixture comprising the acylated compound may be subjected to known separation steps to separate the acylated compound (e.g. extraction with dichloromethane).

30

For example, the reaction temperature may be from 0 to 90°C, preferably 20 to 90 °C. At temperatures below 20°C, the reaction proceeds very slowly and at temperatures of above 90°C, tarring may occur. Preferably, the reaction temperature is chosen to be at least 26 °C and/or at most 50 °C, more preferably at most 30°C. The pressure is preferably atmospheric pressure (1 bar). The duration of the reaction (stirring) may for example be in the range from 1.5 to 4 hours, e.g. 2 to 4 hours.

Preferably, the Lewis acid is selected from the group consisting of a metal halide, a non-metal halide, tungstophosphate, clay and sulphonic acid and preferably step a) is performed at a reaction temperature of 20-30 °C for 1.5 to 4 hours.

Step b)

In step b), the acylated compound obtained by step a) is cyclized with a mineral acid at a reaction temperature to form a corresponding substituted benzinda-1-one compound of formula (2).

The mineral acid may e.g. be sulphuric acid.

Step b) may be performed by an addition of the mineral acid to the acylated compound obtained by step a) or vice versa, followed by stirring at a reaction temperature. Preferably, step b) is performed by adding the mineral acid to the acylated compound obtained by step a), raising temperature of the mixture to a reaction temperature and stirring at the reaction temperature. The obtained mixture comprising the compound of formula (2) may be subjected to known separation steps to separate the compound of formula (2) (e.g. extraction with dichloromethane).

For example, the reaction temperature may be from 40 to 120°C, preferably 80-100 °C, for example around 90°C. The pressure is preferably atmospheric pressure (1 bar). The duration of the reaction (stirring) may e.g. be 0.5-1 hour.

Preferably, the mineral acid is sulphuric acid and preferably step b) is performed at a reaction temperature of 80-100 °C for 0.5-1 hour.

Step c)

In step c), the compound of formula (2) is halogenated with a halogenating agent at a reaction temperature to form a corresponding substituted 2-halo-benzindole-1-one compound of formula (3).

- 5 Halogenation can be carried out e.g. with a brominating or an iodinating agent.

Iodination can be carried out with any organic and inorganic iodinating agent. Inorganic iodinating agent may e.g. be sodium iodide or iodine. The organic iodinating agent may e.g. be methyl iodide.

10

Bromination can be carried out with any organic and inorganic brominating agent. Preferably an organic brominating agent is used such as ammonium tribromide salt, for example pyridinium tribromide or phenyltrimethylammoniumtribromide. Other examples of suitable halogenating agent include bromine, N-bromosuccinimide and 1,3-dibromo-5,5-dimethylhydantoin.

15

The halogenation of step c) may in principle be performed in any solvent known to be suitable for halogenation. Preferably, organic solvents are used. Examples of the solvent include alcohols, for example methanol or ethanol; aromatic solvents, for example
20 benzene, toluene, xylene; ethers for example tetrahydrofuran, diethyl ether, dioxane or dimethoxy ethane; amides for example dimethylformamide and combinations thereof. Particularly preferred are ethers such as tetrahydrofuran.

20

Step c) may be performed by an addition of compound (2) to the halogenating agent or
25 vice versa, followed by stirring at a reaction temperature. Preferably, step c) is performed by adding a solution of the compound (2) in a solvent to a solution of the halogenating agent in a solvent, raising the temperature of the mixture to a reaction temperature and stirring at the reaction temperature. The temperature, pressures and reaction time known to be suitable for halogenation by the person skilled in the art may be used. Optimal
30 conditions can be found using routine experimentation. The obtained mixture comprising the compound (3) may be subjected to known separation steps to separate the compound (3) (e.g. extraction with diethyl ether).

30

For example, the reaction temperature may be from 0 to 120°C, preferably 20 to 120 °C. The addition of compound (2) to the halogenating agent may be performed at a lower temperature (e.g. at 0-5 °C) than the reaction temperature during the subsequent stirring. At temperatures below 20°C, the reaction proceeds very slowly and at temperatures of
5 above 120°C, tarring may occur. Preferably, the temperature is chosen to be at least 26 °C, preferably at least 30 °C and/or at most 100, preferably at most 60°C. The pressure is preferably atmospheric pressure (1 bar). The duration of the reaction (stirring) may for example be in the range from 3-10 hours, e.g. 4-8 hours.

- 10 Preferably, the halogenating agent is a brominating agent or an iodinating agent and preferably step c) is performed at a reaction temperature of 20-30 °C for 3-10 hours.

Step d)

- 15 In step d), the compound of formula (3) is reduced with a reducing agent at a reaction temperature to form a corresponding substituted 2-halo-benzinda-1-ol of formula (4).

The reduction of step d) may be carried out with any organic and inorganic reducing agent. Preferably an inorganic agent is used such as hydrides, for example sodium borohydride or lithium aluminium hydride. Particularly preferred is sodium borohydride.

20

- The reduction of step d) may in principle be performed in any solvent known to be suitable for reduction. Preferably, organic solvents are used. Examples of the solvent include alcohols, for example methanol or ethanol; aromatic solvents, for example benzene, toluene, xylene; ethers for example tetrahydrofuran, diethyl ether, dioxane or dimethoxy
25 ethane; amides for example dimethylformamide and combinations thereof. Particularly preferred is a mixture of an ether such as tetrahydrofuran and an alcohol such as methanol.

- 30 Step d) may be performed by an addition the reducing agent to compound (3) or vice versa, followed by stirring at a reaction temperature. Preferably, step d) is performed by adding the reducing agent to a solution of the compound (3) in a solvent, raising the temperature of a mixture to a reaction temperature and stirring at the reaction temperature. At the end of the reaction, an acid such as hydrochloric acid may be added to the reaction mixture. The temperature, pressures and reaction time known to be suitable by the person

skilled in the art for reduction may be used and optimal conditions can be found using routine experimentation. The obtained mixture comprising the compound (4) may be subjected to known separation steps to separate the compound (4) (e.g. extraction with dichloromethane).

5

For example, the reaction temperature may be from 0 to 80°C, preferably 40 to 120 °C. The addition of the reducing agent to the compound of formula (3) may be performed at a lower temperature (e.g. at 0-5 °C) than the temperature at the subsequent stirring. At temperatures below 20°C, the reaction proceeds very slowly and at temperatures of above 120°C, tarring may occur. Preferably, the temperature is chosen to be at least 26 °C, and/or at most 100 °C, preferably at most 30°C. The pressure under which the process is performed is preferably atmospheric pressure (1 bar). The duration of the reaction (stirring) may for example be in the range from 10 min to 2 hours.

10

15 Preferably, the reducing agent is a hydride and preferably step d) is performed at a reaction temperature of 20-30 °C for 10 minutes to 2 hours.

Step e)

20

The compound of formula (4) is dehydrated by a dehydration agent at a reaction temperature to obtain the substituted 2-halo-benzindene compound of formula (5).

Dehydration can be carried out with any organic and inorganic acid. Inorganic acids may e.g. be sulphuric acid or phosphoric acid. Organic acids may e.g. be *p*-toluenesulphonic acid.

25

The dehydration of step e) may in principle be performed in any solvent known to be suitable for dehydration. Preferably, organic solvents are used. Examples of the solvent include aromatic solvents, for example benzene, toluene, xylene; ethers for example tetrahydrofuran, diethyl ether, dioxane or dimethoxy ethane; amides for example dimethylformamide and combinations thereof. Particularly preferred are aromatic solvents such as toluene.

30

Step e) may be performed by an addition of the dehydration agent to compound (4) or vice versa, followed by stirring at a reaction temperature. Preferably, step e) is performed by

addition of the dehydration agent to a solution of the compound (4) in a solvent, raising the temperature of the mixture to a reaction temperature and stirring at the reaction temperature. The temperature, pressures and reaction time known to be suitable by the person skilled in the art for dehydration may be used and optimal conditions can be found using routine experimentation.

For example, the reaction temperature may be from 60 to 140 °C. At temperatures below 60 °C, the reaction proceeds very slowly and at temperatures of above 140 °C, tarring may occur. Preferably, the temperature is chosen to be at least 80 °C, more preferably at least 110 °C and/or at most 125 °C, preferably at most 110 °C. The pressure under which the process is performed is preferably reflux pressure of solvents. The duration of the reaction (stirring) may for example be in the range from 10 min to 2 hours.

Preferably, the dehydration agent is an organic acid or an inorganic acid and at a reaction temperature of 60-140 °C for 3-10 hours.

Further processes

The present invention further relates to a process for the preparation of a metallocene complex comprising the process for the preparation of the substituted 2-halo-benzindene compound according to the invention and providing the metallocene complex from the substituted 2-halo-benzindene compound. The process for the preparation of the metallocene complex comprises reacting the substituted 2-halo-benzindene compound with a suitable compound to obtain the desired metallocene complex. For example, the substituted 2-halo-benzindene compound may be reacted with e.g. dibenzo[c,e][1,2,7]oxadiborepine-5,7-diol to obtain 2,2'-Biphenyl-2,2'-diylbis-3H-cyclopenta[a]naphthalene, which in turn may be reacted with ZrCl₄ to obtain a metallocene complex [2,2'-Di-(η⁵-cyclopenta[a]naphthalen-2-yl)biphenyl]zirconium dichloride.

The present invention further relates to a process for the preparation of a catalyst comprising the process for the preparation of the metallocene complex according to the invention and

- reacting a solution of a co-catalyst in a solvent with the metallocene complex to form a pre-catalyst solution,

- adding the pre-catalyst solution to an inorganic support material to form a pre-catalyst mixture and
- stirring the pre-catalyst mixture at an elevated temperature under vacuum to form the catalyst.

5

The present invention further relates to a process for the preparation of a catalyst comprising the process for the preparation of the metallocene complex according to the invention and

- adding a solution of a co-catalyst in a solvent to an inorganic support material to give a treated support,
- adding a metallocene complex to the treated support to give a pre-catalyst mixture
- stirring the pre-catalyst mixture at an elevated temperature under vacuum to form the catalyst.

15 The catalyst may be used e.g. in a solution polymerization of olefins. The olefin to be polymerized can be one type of olefin or can be mixtures of different olefins. The polymerization thus includes homopolymerization and copolymerization. Examples of olefins are ethylene and α -olefins such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene and styrene; conjugated and non-

20 conjugated dienes such as butadiene, 1,4-hexadiene, 5-ethylidene-2-norbornene, dicyclopentadiene, 4-methyl-1,4-hexadiene and 7-methyl-1,6-octadiene; and cyclic olefins such as cyclobutene, but is not limited thereto. The α -olefins may optionally contain heteroatoms, like for example O, N, S and P.

25 The co-catalyst employed according to the present invention can be an aluminium- or boron-containing co-catalyst. Suitable aluminium-containing co-catalysts comprise aluminoxanes and alkyl aluminium. The aluminoxanes usable according to the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl aluminoxanes represented by the formula: $R^6 - (AlR^6 - O)_n - AlR^6_2$ for oligomeric, linear aluminoxanes and $(- AlR^6 - O -)_m$ for oligomeric, cyclic aluminoxanes; wherein n is 1-40,

30 preferably n is 10-20; m is 3-40, preferably m is 3-20 and R^6 is a C_1 to C_8 alkyl group and preferably a methyl group. Further other organoaluminum compounds can be used such as trimethylaluminum, triethylaluminium, triisopropylaluminum, tri-n-propylaluminum, triisobutylaluminum, tri-n-butylaluminum, triamylaluminium; dimethylaluminium ethoxide,

diethylaluminium ethoxide, diisopropylaluminium ethoxide, di-n-propylaluminium ethoxide, diisobutylaluminium ethoxide and di-n-butylaluminium ethoxide; dimethylaluminium hydride, diethylaluminium hydride, diisopropylaluminium hydride, di-n-propylaluminium hydride, diisobutylaluminium hydride, di-n-butylaluminium hydride and
5 tetra-isobutyl-aluminoxane.

Suitable boron-containing co-catalysts include perfluorophenylboranes and/or perfluorophenylborates as described for instance by Chen, E., Marks, T., in *Chemical Reviews* **2000**, *100*, 1391-1434.

10

Preferably, the co-catalyst is an organoaluminum co-catalyst. More preferably, methylaluminoxane (MAO) is used as the co-catalyst.

15

In a preferred embodiment, the catalyst comprises an inorganic support material. When a support material is present, the support material is preferably an inert support material, more preferably a porous inert support material. Examples of porous inert support materials are talc and inorganic oxides. Preferably, the support material is in a finely divided form.

20

Suitable inorganic oxide materials include group 2A, 3A, 4A and 4B metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica or alumina are magnesia, titania, zirconia and the like. Preferably, the catalyst comprises a support material and the support material is alumina or silica, more preferably a silica, most preferably a silica having a surface area
25 between 200 and 900 m²/g and a pore volume between 0.5 and 4 ml/g.

30

The preferred Al/Zr molar ratio to be employed in the process for preparing the metallocene complex is between 10 and 1000, more preferably between 50 and 500, most preferably between 75 and 300.

The elevated temperature for forming the catalyst may be a temperature between 20 and 150 °C, preferably between 40 and 100 °C.

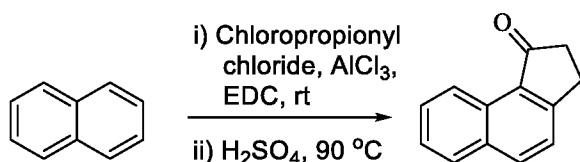
It is noted that the invention relates to all possible combinations of features described herein, preferred in particular are those combinations of features that are present in the claims. It will therefore be appreciated that all combinations of features relating to the composition according to the invention; all combinations of features relating to the process according to the invention and all combinations of features relating to the composition according to the invention and features relating to the process according to the invention are described herein.

It is further noted that the term 'comprising' does not exclude the presence of other elements. However, it is also to be understood that a description on a product/composition comprising certain components also discloses a product/composition consisting of these components. The product/composition consisting of these components may be advantageous in that it offers a simpler, more economical process for the preparation of the product/composition. Similarly, it is also to be understood that a description on a process comprising certain steps also discloses a process consisting of these steps. The process consisting of these steps may be advantageous in that it offers a simpler, more economical process.

The invention is now elucidated by way of the following examples, without however being limited thereto.

Examples

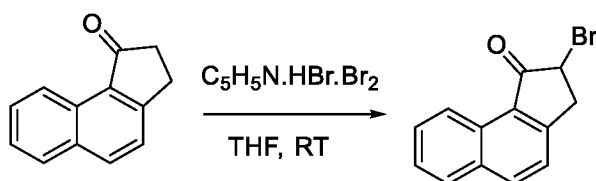
1.1 Synthesis of 2,3-dihydro-1H-cyclopenta[α]naphthalen-1-one, compound of formula (2) (wherein R1, R2, R3, R4, R7 and R8 all stand for H)



In a flask equipped with a magnetic stirrer, a solution of naphthalene (50 g, 0.39 mol) in ethylene dichloride (200 mL) was gradually added to a solution of 3-chloropropionyl chloride (37.5 mL, 0.39 mol) and aluminium chloride (65 g) in ethylene dichloride (100 mL) at room temp. After 2 h of stirring at room temperature, the ethylene dichloride layer was

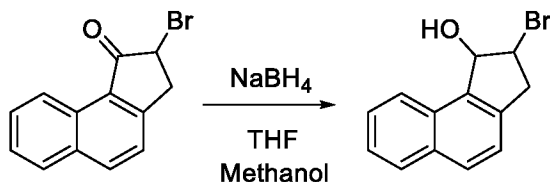
poured on 200 g of crushed ice and was extracted with dichloromethane. The combined organic extract was washed by aq K_2CO_3 , dried on sodium sulphate and filtered. Finally the solvent was evaporated on rota vac under reduced pressure. To the residual oil obtained, concentrated H_2SO_4 (100 mL) was added dropwise, and the mixture was heated at 90° C for 40 min. After being cooled to room temperature, the mixture was poured slowly on 500 g of crushed ice and the reaction mixture was extracted with DCM. The combined organic layers were washed with water, saturated aq $NaHCO_3$, brine, dried over Na_2SO_4 , and filtered, and the volatiles were removed in vacuo (43 g, 61% yield)

- 1.2 Synthesis of 2-bromo-2,3-dihydro-1H-cyclopenta[α]naphthalen-1-one, compound of formula (3) (wherein R1, R2, R3, R4, R7 and R8 all stand for H and X is Br)



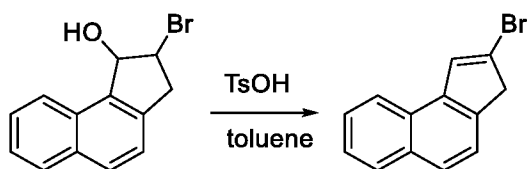
- To a cold THF (25 mL) solution (0°C) of pyridinium tribromide (3.5 g, 0.01 mol), the THF (25 mL) solution of 2,3-Dihydro-1H-cyclopenta[α]naphthalen-1-one (2 g, 0.01 mol) was added slowly. Then the temperature was raised to room temperature and the reaction mixture was stirred for 8 h. A formation of white crystalline solid is observed at the end of the reaction. To this reaction mass, water (100 mL) was added and the mixture was extracted with diethyl ether, dried over anhydrous Na_2SO_4 , filtered and evaporated to dryness resulting in yellow oil. To the yellow oil ethanol was added and compound was precipitated at -20 °C to obtain yellow solid 1.9 gm (66% yield).

- 1.3 Synthesis of 2-Bromo-2,3-dihydro-1H-cyclopenta[α]naphthalen-1-ol, compound of formula (4) (wherein R1, R2, R3, R4, R7 and R8 all stand for H and X is Br)



To a solution of 2-bromo-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (1.5 g, 0.005 mol) in THF (16 mL) and methanol (8 mL), sodium borohydride (0.23 g, 0.006 mol) was added slowly at 0 °C. There is evolution of gas from reaction mixture during addition. Then the ice bath was removed and the reaction was stirred for 1h at room temperature. Finally, a solution of hydrochloric acid in water (2.5%, 25 mL) was added to the reaction mixture. Then the reaction mixture was extracted with dichloromethane (2 x 20 mL). The combined organic phases were dried over sodium sulfate and filtered. The organic solvents were removed under reduced pressure to give 1.4 g (93% yield) of 2-bromo-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ol.

1.4 Synthesis of 2-Bromo-3H-cyclopenta[α]naphthalene, compound of formula (5) (wherein R1, R2, R3, R4, R7 and R8 all stand for H and X is Br)

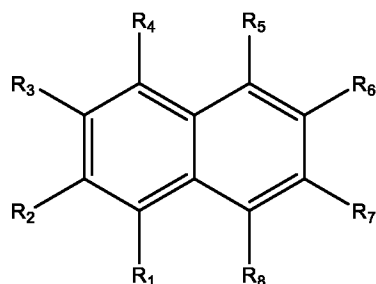


To a solution of 2-bromo-2,3-dihydro-1H-cyclopenta[α]naphthalen-1-ol (1.4 g, 0.005 mol) in warm toluene (10 mL), *p*-toluenesulfonic acid (0.18 g, 0.0009 mol) was added. The mixture was heated to reflux for 30 min with Dean-Stark trap to remove water. Then the mixture was cooled to room temperature and washed with sat Na₂CO₃ solution and water. The organic fraction was dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel 60-120 (eluent: hexane/ethyl acetate) to give 0.68 g (52% yield).

CLAIMS

1. A process for the preparation of a substituted 2-halo-benzindene compound, comprising the steps of:

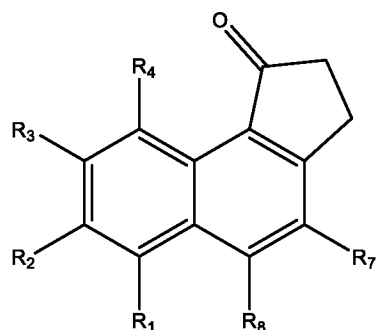
- 5 a) Friedel Crafts acylation of an aromatic compound of formula (1) with 3-chloropropionyl chloride in the presence of a Lewis acid to form a corresponding acylated compound,



formula (1)

10 wherein R1, R2, R3, R4, R5, R6, R7, R8 each independently stands for H, a hydrocarbon radical having 1-20 carbon atoms, a halide, an alkoxy having 1-6 C atoms, an alkyl sulphide, an amine, a Si or B-containing group or a P-containing group;

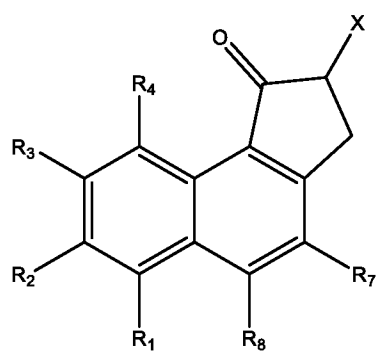
- b) cyclization of the acylated compound with a mineral acid to form a corresponding substituted benzinda-1-one compound of formula (2)



formula (2)

15 wherein R1, R2, R3, R4, R7, R8 are as described for formula (1);

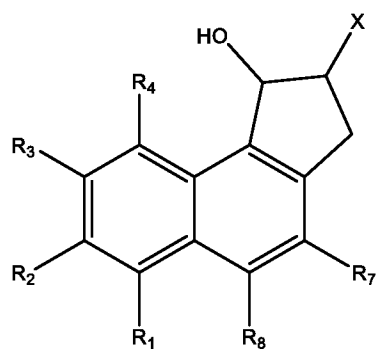
- c) halogenation of compound of formula (2) with a halogenating agent to form a corresponding substituted 2-halo-benzinda-1-one compound of formula (3).



formula (3)

wherein R1, R2, R3, R4, R7, R8 are as described for formula (1) and X is halogen;

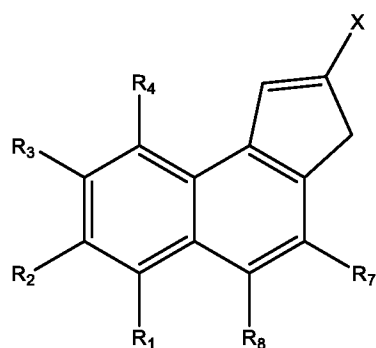
d) reduction of compound of formula (3) with a reducing agent to form a corresponding substituted 2-halo-benzinda-1-ol (4)



formula (4)

wherein R1, R2, R3, R4, R7, R8 are as described for formula (1) and X is halogen;

e) dehydration of compound of formula (4) with a dehydration agent to obtain the substituted 2-halo-benzindene compound of formula (5)



formula (5).

2. The process according to claim 1, wherein R1, R2, R3, R4, R5, R6, R7, R8 each stands for H.
3. The process according to any one of the preceding claims, wherein X stands for Br.

4. The process according to any one of the preceding claims, wherein the Lewis acid is selected from the group consisting of a metal halide, a non-metal halide, tungstophosphate, clay and sulphonic acid and preferably step a) is performed at a reaction temperature of 20-30 °C for 1.5 to 4 hours.
5. The process according to any one of the preceding claims, wherein the mineral acid is sulphuric acid and preferably step b) is performed at a reaction temperature of 80-100 °C for 0.5-1 hour.
- 10 6. The process according to any one of the preceding claims, wherein the halogenating agent is a brominating agent or an iodinating agent and preferably step c) is performed at a reaction temperature of 20-30 °C for 3-10 hours.
- 15 7. The process according to any one of the preceding claims, wherein the reducing agent is a hydride and preferably step d) is performed at a reaction temperature of 20-30 °C for 10 minutes to 2 hours.
- 20 8. The process according to any one of the preceding claims, wherein the dehydration agent is an organic acid or an inorganic acid and preferably step e) is performed at a reaction temperature of 60-140 °C for 3-10 hours.
- 25 9. A process for the preparation of a metallocene complex comprising the process for the preparation of the substituted 2-halo-benzindene compound according to any one of claims 1-8 and providing the metallocene complex from the substituted 2-halo-benzindene compound.
- 30 10. A process for the preparation of a catalyst for a solution polymerization of olefins, comprising the process for the preparation of the metallocene complex according to the claim 9 and
reacting a solution of a co-catalyst in a solvent with the metallocene complex to form a pre-catalyst solution,
adding the pre-catalyst solution to an inorganic support material to form a pre-catalyst mixture and
35 stirring the pre-catalyst mixture at an elevated temperature under vacuum to form the catalyst.

11. A process for the preparation of a catalyst for a solution polymerization of olefins, comprising the process for the preparation of the metallocene complex according to the claim 9 and
- 5 adding a solution of a co-catalyst in a solvent to an inorganic support material to give a treated support,
- adding a metallocene complex to the treated support to give a pre-catalyst mixture and
- stirring the pre-catalyst mixture at an elevated temperature under vacuum to form the catalyst.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/077548

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C23/38
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	A. S. LUBBE ET. AL.: "Control of Rotor Function in Light-Driven Molecular Motors", JOURNAL OF ORGANIC CHEMISTRY, vol. 76, 19 September 2011 (2011-09-19), pages 8599-8610, XP002775585, DOI: 10.1021/jo201583z page 8600 Scheme 1 -----	1-11
Y	E. G IJPEG ET. AL.: "A Suzuki Coupling Based Route to 2,2'-Bis(2-indenyl)biphenyl Derivatives.", JOURNAL OF ORGANIC CHEMISTRY, vol. 67, 13 December 2001 (2001-12-13), pages 169-176, XP002775586, DOI: 10.1021/jo016040i cited in the application page 174, Scheme 4 -----	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"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

15 November 2017

Date of mailing of the international search report

12/12/2017

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