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(54) Title: PROCESS FOR THE PREPARATION OF 1-(3,5-DICHLORO-4-FLUORO-PHENYL)-2,2,2-TRIFLUORO-ETHANONE

(57) Abstract: The invention relates to a process for the preparation of a compound of formula I comprising a) reacting a compound of formula II in the presence of magnesium or an organometallic reagent of formula III RIM₂X (III), wherein R is C₁₋₅ alkyl; M² is Li or Mg and X is halogen or absent; with a compound of formula IV CF₃-C(0)-R₂ (IV), wherein R₂ is halogen, hydroxyl, C₁₋₅ alkyl, (di-G-C₅ alkoxy), (di-G-C₅ alkoxy)amino, OC(0)CF₃, phenoxy or OM; wherein M₁ is Lithium, Magnesium, Sodium or Potassium; to a compound of formula V, and b) reacting the compound of formula V with alkali metal fluoride in the presence of catalytic amounts of a phase transfer catalyst in the presence of a polar solvent to the compound of formula I.

\[
\text{(I)}
\]

\[
\text{(II)}
\]

\[
\text{(V)}
\]

— of inventorship (Rule 4.17(iv))

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

Declarations under Rule 4.17:
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(H))
Process for the preparation of 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone

The present invention relates to the preparation of 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone using 5-bromo-1,2,3-trichloro-benzene as a starting material.

1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone is an important intermediate for the preparation of pesticidally active isoxazoline-substituted benzamides as for example disclosed in EP 1932836A1.

1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone can be advantageously prepared by using 5-bromo-1,2,3-trichloro-benzene as a starting material. 5-bromo-1,2,3-trichloro-benzene can be prepared as described in Narander, N.; Srinivasu, P.; Kulkarni, S.J.; Raghavan, K.V. Synth. Comm. 2000, 30, 3669 and Sott, R.; Hawner, C.; Johansen, J.E. Tetrahedron 2008, 64, 4135. 3-Trifluoromethyl chalcones can be prepared according to methods disclosed in WO 2009/12668.

The synthesis of aryltrifluormethyl ketones by reacting derivatives of trifluoroacetic acid with organometallic reagents derived from haloarenes is well known and for example described in WO 2012/120135 for the preparation of 2,2,2-trifluoro-1-(3,4,5-trichlorophenyl)ethanone. For the synthesis of 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone the corresponding starting material is 5-bromo-1,3-dichloro-2-fluoro-benzene. However, this substance is difficult to prepare in particular on a large scale with the only described synthesis being an inefficient multistep approach described in Miller, M.W.; Mylari, B.L.; Howes, H.L.; Figdor, S.K.; Lynch, M.J.; Lynch, J.E.; Koch, R.C. J. Med. Chem. 1980, 23, 1083, CN 101177379, WO 2009/070485 and CN 103664511 (Scheme 1).

Scheme 1

Therefore, it is highly desirable to prepare 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone from the more easily accessible 2,2,2-trifluoro-1-(3,4,5-trichlorophenyl)ethanone. Surprisingly, it was found that reacting 2,2,2-trifluoro-1-(3,4,5-trichlorophenyl)ethanone with potassium fluoride in the presence of a phase transfer catalyst and a polar solvent provided the desired 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-
trifluoro-ethanone. While such nucleophilic aromatic substitution reactions are well known for nitroaromatic compounds (as for example disclosed in WO 92/00270) there is no prior art describing comparable reactions with trifluoromethyl ketones since this group is in general not known to be a sufficiently strong activating group.

It is therefore the object of the present invention to provide a process for the preparation of 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone using 5-bromo-1,2,3-trichloro-benzene as an intermediate. The process according to the invention is characterized by a reduced number of reaction steps and high selectivity and yield.

Thus, according to the present invention, there is provided a process for the preparation of the compound of formula I

![Chemical Structure I](image)

comprising

a) reacting the compound of formula II

![Chemical Structure II](image)

in the presence of magnesium or an organometallic reagent of formula III

![Chemical Structure III](image)

wherein

- \(R_1\) is \(C_1-C_4\)alkyl;
- \(M^2\) is Lithium or Magnesium and
- \(X\) is halogen or absent;
- with a compound of formula IV

![Chemical Structure IV](image)

wherein

- \(R_2\) is halogen, hydroxyl, \(C_1-C_2\)alkoxy, \((d\,C_1-C_2\)alkyl)amino, \(OC(0)CF_3\), phenoxy or \(OM^1\); wherein \(M^1\) is Lithium, Magnesium, Sodium or Potassium;
- to the compound of formula V,
and

b) reacting the compound of formula V with an alkali metal fluoride in the presence of catalytic amounts of a phase transfer catalyst in the presence of a polar solvent to the compound of formula I.

The alkyl groups occurring in the definitions of the substituents can be straight-chain or branched and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl or tert-butyl. Alkoxy is, for example, methoxy, ethoxy, propoxy, i-propoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy. The following scheme describes the reactions of the invention in more detail.

Scheme 2

Step a)

The compound of formula V can be prepared by reacting a compound of formula II first with magnesium then with a compound of formula IV

\[ \text{CF}_3\text{C(O)R}_2 \text{ (IV)}, \]

wherein \( R_2 \) is halogen, hydroxyl, \( \text{C}_1\text{-C}_4 \text{alkoxy}, (\text{di-C}_1\text{-C}_4 \text{alkyl}) \text{amino}, \text{OC(O)}\text{CF}_3, \text{phenoxy} \) or \( \text{OM}^1 \); wherein \( M^1 \) is Lithium, Magnesium, Sodium or Potassium; Alternatively, the compound of formula V can be prepared by reacting a compound of formula II first with an organometallic reagent of formula III

\[ \text{R}_1\text{-M}^2\text{X (III)}, \]

wherein

\[ \text{R}_1 \text{ is C}_1\text{-C}_4 \text{alkyl; } \]

\( M^2 \) is Lithium or Magnesium and

\( X \) is halogen or absent; and then with
the compound of formula IV

\[ \text{CF}_3\text{C(0)R}_2 \] (IV),

wherein \( R_2 \) is halogen, hydroxyl, C\(_{1-2}\)alkoxy, (di-C\(_{1-2}\)alkyl)amino, \( \text{OC}(0)\text{CF}_3 \), phenoxy or OM\(^1 \); wherein M\(^1 \) is Lithium, Magnesium, Sodium or Potassium. The compound of formula III is preferably used in form of a complex with LiCl.

Typically the reaction is performed in an aprotic organic solvent. Suitable solvents include but are not limited to organic ethers such as tetrahydrofuran, 2-methyl-tetrahydrofuran, 1,4-dioxane, diethyl ether, t-butyldimethyl ether and hydrocarbons such as toluene, benzene, hexane and cyclohexane. The reaction can be carried out at a temperature from -80 °C to 50 °C, preferably from -20 °C to 25 °C.

**Step b)**:
The compound of formula I can be prepared by reaction of a compound of formula V with an alkali metal fluoride in the presence of a phase transfer catalyst. Suitable metal fluorides include KF, LiF and NaF. Suitable phase transfer catalysts include phosphonium salts of general formula \( (\text{R}_3\text{P})_4\text{X} \) and ammonium salts of general formula \( (\text{R}_3\text{N})_4\text{X} \) where \( \text{R}_3 \) is C\(_{1-2}\)alkyl or phenyl and \( X \) is halogen. Phosphonium salts are preferred.

Typically the reaction is performed in an organic solvent or mixtures thereof. Suitable solvents are polar in nature and include, but are not limited to sulfolane, dimethylformamide and dimethylsulfoxide.

The reaction can be carried out at a temperature from 100 °C to 250 °C, preferably from 120 °C to 160 °C.

A preferred embodiment of the process of the invention comprising

a) reacting the compound of formula II

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Br}
\end{array}
\] (II),

in the presence of an organometallic reagent of formula III

\[ \text{R}_1\text{M}^2\text{X} \] (III),

wherein

R\(_1\) is C\(_{1-2}\)alkyl;
M\(^2 \) is Lithium or Magnesium and
X is halogen or absent;
with a compound of formula IV

\[ \text{CF}_3\text{C(0)-R}_2 \text{ (IV)} \]

wherein \( R_2 \) is halogen, hydroxyl, \( \text{C}_1\text{-C}_2\text{alkoxy} \), \( \text{C}_1\text{-C}_4\text{alkylamino} \), \( \text{OC}_3\text{(O)CF}_3 \), phenoxy or \( \text{OM} \); wherein \( M \) is Lithium, Magnesium, Sodium or Potassium;

to the compound of formula V,

![Formula V](image)

and

b) reacting the compound of formula V with metal fluoride selected from KF, LiF and NaF in the presence of catalytic amounts of a phase transfer catalyst selected from the group consisting of phosphonium salts of general formula \( (\text{R}_3)_4\text{PX} \) and ammonium salts of general formula \( (\text{R}_3)_4\text{NX} \) wherein \( \text{R}_3 \) is \( \text{C}_1\text{-C}_4\text{alkyl} \) or phenyl and \( X \) is halogen; in the presence of a polar solvent selected from the group consisting of sulfolane, dimethylformamide and dimethylsulfoxide, to the compound of formula I. In said preferred embodiment of the invention, the organometallic reagent is isopropylmagnesiumchloride complexed with LiCl.

**Preparatory examples:**

**Example 1: Preparation of 2,2,2-trifluoro-1-(3,4,5-trichlorophenyl)ethanone of formula V:**

![Formula V](image)

To a solution of 5-bromo-1,2,3-trichloro-benzene (220 g, 811 mmol) in tetrahydrofuran (1600 ml) was added 1.3 M iPrMgCl-LiCl in THF (1250 ml, 1622 mmol) slowly at 20 °C. The reaction mixture was stirred for 2 hours and cooled to 0 °C. Methyl 2,2,2-trifluoroacetate (31.48 g, 2434 mmol) was added slowly and the reaction mixture was stirred at ambient temperature for 1 hour. The reaction mixture was cooled to 0 °C and 2.0 M HCl (810 ml, 1622 mmol) was added dropwise during 30 min. The resulting mixture was diluted with ethyl acetate, the organic layer was washed with brine, dried over anhydrous MgSO₄ and evaporated under reduced pressure. The crude product was dissolved in a minimum amount of cyclohexane and the solution was cooled to -10 °C. The formed precipitate was filtered off to afford 2,2,2-trifluoro-1-(3,4,5-trichlorophenyl)ethanone (122 g) as a yellow solid. The filtrate was diluted with
cyclohexane and washed twice with acetonitrile. Cyclohexane phase was evaporated under reduced pressure and the residue was dissolved in a minimum amount of cyclohexane. The solution was cooled to -10 °C and another portion of 2,2,2-trifluoro-1-(3,4,5-trichlorophenyl)ethanone (35 g) was filtered off.

$^1$H NMR (400MHz, CDCl$_3$) δ 8.07-8.05 (m, 2H).

Example 2: Preparation of 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone of formula I:

To a solution of 2,2,2-trifluoro-1-(3,4,5-trichlorophenyl)ethanone (1.0 g, 3.6 mmol) in sulfolane (3 ml) was added dry potassium fluoride (0.35 g, 4.32 mmol) and tetraphenylphosphonium bromide (0.015 g, 0.036 mmol). The resulting reaction mixture was stirred at 160 °C for 5 hours. The reaction mixture was distilled under reduced pressure. Fractions containing the product were further purified with silica gel chromatography (eluting with pure heptane) to afford 1-(3,5-dichloro-4-fluoro-phenyl)-2,2,2-trifluoro-ethanone (0.571 g) as a colorless oil and a mixture of ketone and hydrate forms (ca 3:1).

$^{19}$F NMR (400MHz, CDCl$_3$) δ -71.5, -84.7, -102.4, -112.9.
Claims:

1. A process for the preparation of the compound of formula I

\[
\begin{align*}
&\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} \\
&\text{F} & \text{F} & \text{Cl} & \text{F} \\
(I), \\
\end{align*}
\]

comprising

a) reacting the compound of formula II

\[
\begin{align*}
&\text{Cl} & \text{Cl} & \text{Cl} & \text{Br} \\
\end{align*}
\]

(II),

in the presence of magnesium or an organometallic reagent of formula III

5

wherein

\[R_1-M^2X\] (III),

\[R_1\] is C_1-C_4 alkyl;
\[M^2\] is Lithium or Magnesium and
\[X\] is halogen or absent;

10

with a compound of formula IV

\[
\begin{align*}
&\text{CF}_3 & \text{C}(0)-R_2 \\
(IV), \\
\end{align*}
\]

wherein \[R_2\] is halogen, hydroxyl, C_1-C_4 alkoxy, (di-C_1-C_4 alkyl)amino, OC(0)CF_3, phenoxy or OM'; wherein
\[M'\] is Lithium, Magnesium, Sodium or Potassium;

15

to the compound of formula V,

\[
\begin{align*}
&\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} \\
&\text{F} & \text{F} & \text{Cl} & \text{F} \\
(V), \\
\end{align*}
\]

and

b) reacting the compound of formula V with an alkali metal fluoride in the presence of catalytic amounts of a phase transfer catalyst in the presence of a polar solvent to the compound of formula I.

20

25
2. A process according to claim 1, comprising
   a) reacting the compound of formula II

   \[
   \begin{array}{c}
   \text{Cl} \\
   \text{Cl} \\
   \text{Cl} \\
   \text{Br}
   \end{array} \\
   \text{(II),}
   \]

   in the presence of an organometallic reagent of formula III

   \[R_1M^2X \text{ (III),}\]

   wherein
   
   \(R_1\) is \(\text{C}_1-\text{C}_4\)alkyl;
   \n   \(M^2\) is Lithium or Magnesium and
   
   \(X\) is halogen or absent.

3. A process according to claim 2, wherein the organometallic reagent is isopropylmagnesium chloride complexed with LiCl.

4. A process according to claim 1, wherein the alkali metal fluoride is selected from KF, LiF and NaF.

5. A process according to claim 1, wherein the phase transfer catalyst is selected from the group consisting of phosphonium salts of general formula \((\text{R}_3)_{4}PX\) and ammonium salts of general formula \((\text{R}_3)_{4}NX\) wherein \(\text{R}_3\) is \(\text{C}_1-\text{C}_4\)alkyl or phenyl and \(X\) is halogen.

6. A process according to claim 1, wherein the polar solvent is selected from the group consisting of sulfolane, dimethylformamide and dimethylsulfoxide.

7. A process according to claim 1, comprising
   a) reacting the compound of formula II

   \[
   \begin{array}{c}
   \text{Cl} \\
   \text{Cl} \\
   \text{Cl} \\
   \text{Br}
   \end{array} \\
   \text{(II),}
   \]

   in the presence of an organometallic reagent of formula III

   \[R_1M^2X \text{ (III),}\]

   wherein
\( R \) is \( \text{C}_4 \text{C}_{\text{alkyl}} \);
\( M^2 \) is Lithium or Magnesium and
\( X \) is halogen or absent;
with a compound of formula \( IV \)
\[
\text{CF}_3\text{C}(\text{O})\text{-R}_2 \quad (IV),
\]
wherein \( \text{R}_2 \) is halogen, hydroxyl, \( \text{C}_1\text{C}_2\text{alkoxy} \), \( \text{(di-} \text{C}_1\text{-C}_2\text{alkyl)}\text{amino}, \text{OC(}0\text{)CF}_3\), phenoxy or OM'\; wherein
\( M^1 \) is Lithium, Magnesium, Sodium or Potassium;
to the compound of formula \( V \),

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Cl} \\
\text{F} \quad \text{F} \\
\text{O} \\
\end{array}
\]

(V).

10 and

b) reacting the compound of formula \( V \) with an alkali metal fluoride selected from KF, LiF and NaF in the presence of catalytic amounts of a phase transfer catalyst selected from the group consisting of phosphonium salts of general formula \( (\text{R}_3)_4\text{PX} \) and ammonium salts of general formula \( (\text{R}_3)_4\text{NX} \) wherein
\( \text{R}_3 \) is \( \text{C}_1\text{-C}_2\text{alkyl or phenyl and X is halogen; in the presence of a polar solvent selected from the group consisting of sulfolane, dimethylformamide and dimethylsulfoxide, to the compound of formula I.} \)

8. A process according to claim 7, wherein the organometallic reagent is isopropylmagnesiumchloride complexed with LiCl.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C45/00 C07C45/63 C07C49/80
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

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<td>wo 2012/035011 AI (BAYER CR0PSCI ENCE AG [DE] ; MIHARA JUN [JP] ; HATAZAWA MAMORU [JP] ; YAMA) 22 March 2012 (2012-03-22) Example Q, step 1; page 112 -----</td>
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search
11 November 2015

Date of mailing of the international search report
27/11/2015

Name and mailing address of the ISA/
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Authorized officer
Österle, Carmen

Form PCT/ISA/210 (second sheet) (April 2005)
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