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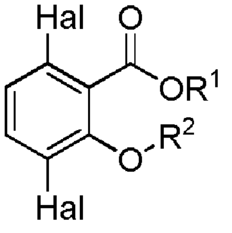
(54) Title: PROCESS FOR PROVIDING DIHALOGEN SUBSTITUTED SALICYLIC ACID DERIVATIVES

(57) Abstract: The present invention relates to a process for providing: a compound of formula (IV): wherein R^1 is hydrogen or -(C_1-C_4)alkyl, R^2 is -(C_1-C_4)alkyl, and each Hal is an independently selected halogen, the process comprising the step of: Reacting a compound of formula (III) wherein R^1 and Hal are defined as above, and R^3 is an alkali metal, in the presence of a Ag(I) compound, a Cu(II) compound, and a compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$.



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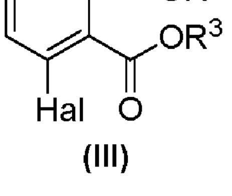

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Process for providing dihalogen substituted salicylic acid derivatives

The present invention relates to a process for providing dihalogen substituted salicylic acid derivatives. In a preferred embodiment, the present invention provides an improved process for the production of the herbicide dicamba (3,6-dichloro-2-methoxybenzoic acid).

Background of the invention

Dicamba is a selective herbicide currently used for treating e.g. corn, wheat or grassland. It kills broadleaf weeds before and after they sprout. The trivial name dicamba refers to the compound 3,6-dichloro-2-methoxybenzoic acid. The estimated global demand for dicamba in 2012 was about 12.000 million tons per year. However, it is expected that the global demand for dicamba will increase significantly.

Dicamba is typically produced on an industrial scale from 2,5-dichlorophenol using carboxylation under Kolbe-Schmitt conditions, methylation and subsequently saponification/acidification. 2,5-Dichorophenol in turn can be obtained from 1,4-dichlorobenzene or 1,2,4-trichlorobenzene. The synthetic route via 1,4-dichlorobenzene involves nitration and subsequent diazotation, and, therefore is undesired for use on an industrial scale. The synthetic route via 1,2,4-trichlorobenzene suffers from limited availability of this starting material and from the formation of several byproducts which are formed in the synthesis of 2,5-dichlorophenol.

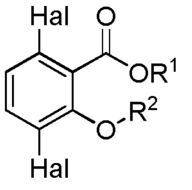
In order to meet the increasing market demand for compounds such as dicamba, there is a need in the art for alternative processes, involving a reduced number of steps and/or improved yield, for providing dihalogen substituted salicylic acid derivatives, especially including dicamba.

The object of the present invention is to meet the above needs. It is a further object of the present invention to implement the improved process for the synthesis of dicamba on an industrial scale. A further object of the present invention is the provision of a cost effective process for the synthesis of dicamba.

Even minor improvements in the yield in reaction sequences for obtaining dicamba would provide a tremendous benefit. For example, an improvement of yield of 1% would provide an additional annual amount 120 million tons of dicamba.

Summary of the invention

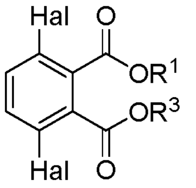
The present invention relates to an improved process for providing dihalogen substituted salicylic acid derivatives using decarboxylative etherification of dihalogenated phtalic acid derivatives. In particular, the present invention relates to a process for providing a compound of formula (IV):



IV

wherein R^1 is hydrogen or $-(C_1\text{-}C_4)$alkyl, R^2 is $-(C_1\text{-}C_4)$alkyl, and each Hal is an independently selected halogen. The process comprises the step of:

Reacting a compound of formula (III)



III

wherein R^1 and Hal are defined as above, and R^3 is an alkali metal, in the presence of a Ag(I) compound, a Cu(II) compound, and a compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$.

In preferred embodiments, the step of reacting the compound of formula (III) is carried out in the further presence of a co-oxidant. The co-oxidant is preferably selected from molecular oxygen (O_2), benzoquinone, $K_2S_2O_8$, $Na_2S_2O_8$, and a peroxyacetic acid ester. More preferably, the co-oxidant is O_2.

Furthermore, the Ag(I) compound is in preferred embodiments selected from Ag_2CO_3, Ag(I) acetate (AgOAc), and Ag_2O. More preferably, the Ag(I) compound is Ag_2CO_3.

In another preferred embodiment, the Cu(II) compound is selected from Cu(II) acetate, and $CuBr_2$. More preferably, the Cu(II) compound is Cu(II) acetate ($Cu(OAc)_2$).

It is further preferred according to the present invention that the compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$ is $Si(OR^2)_4$.

In a further preferred embodiment, the Ag(I) compound is present in an amount of about 0.1 to about 1.0 molar equivalents per one molar equivalent of the compound of formula (III). More preferably, the Ag(I) compound is present in an amount of about 0.25 to about 1.0 molar equivalents per one molar equivalent of the compound of formula (III). In a still further preferred embodiment, the Ag(I) compound is present in an amount of about 0.25 molar equivalents.

It is preferred according to the present invention that the Cu(II) compound is present in an amount of about 0.1 to about 1.0 molar equivalents per one molar equivalent of the compound of formula (III). More preferably, the Cu(II) compound is present in an amount of about 0.2 to about 1.0 molar equivalents per one molar equivalent of the compound of formula (III), still further preferably in an amount of about 1.0 molar equivalent.

Furthermore, the compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$ is preferably present in an amount of about 1.0 to about 5.0 molar equivalents per one molar equivalent of the compound of formula (III). More preferably, the compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$ is present in an amount of about 5.0 molar equivalents.

According to preferred embodiments, the co-oxidant is present in an amount of about 0.8 to about 1.2 molar equivalents per one molar equivalent of the compound of formula (III). More preferably, the co-oxidant is present in an amount of about 1.0 molar equivalent per one molar equivalent of the compound of formula (III). In alternative preferred embodiments, the co-oxidant is O_2 and is provided is gaseous form. In these embodiments, which are especially preferred according to the invention, O_2 is provided at a pressure of about 100 kPa to about 200 kPa, more preferably about 101.3 kPa.

The above step of reacting the compound of formula (III) is carried preferably out at a temperature of about 100°C to about 160°C. More preferably, the step of reacting the compound of formula (III) is carried out at a temperature of about 115°C to about 150°C, still more preferably about 120°C to about 145°C.

Compounds of formula (IV), in which R^1 is $-(C_1\text{-}C_4)$alkyl, can be converted according to the invention to compounds of formula (IV), in which R^1 is hydrogen.

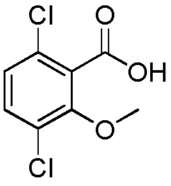
According to the invention, Hal is preferably selected from –F, –Cl, –Br and –I, more preferably –Cl and –Br, and most preferably –Cl.

Furthermore, R^1 is selected from hydrogen, methyl and ethyl, more preferably hydrogen. In certain preferred embodiments according to the invention, R^1 is $-(C_1\text{-}C_4)$alkyl, such as methyl or ethyl, in the compound of formula (III), and the resulting compound of formula (IV), in which R^1 is likewise $-(C_1\text{-}C_4)$alkyl, is preferably converted to a compound of formula (IV), in which R^1 is hydrogen.

R^2 is according to the invention preferably selected from methyl and ethyl, more preferably from methyl.

Furthermore, R^3 is preferably selected from lithium, sodium and potassium, more preferably from sodium and potassium, and most preferably is potassium.

In particular preferred embodiments, the processes according to the present invention are employed for obtaining dicamba. In these preferred embodiments, the compound of formula (IV) finally obtained is



Dicamba

Further preferred embodiments of the present invention are apparent from the following detailed description and the attached claim set.

Detailed Description of the Invention

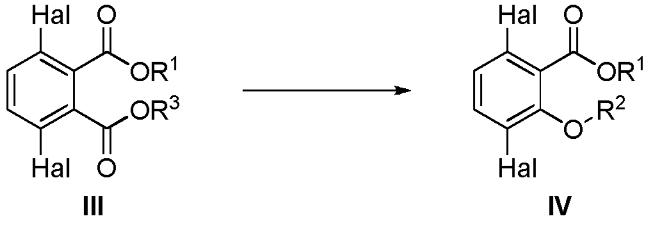
In the following, illustrative embodiments of the present invention are described in more detail.

The term “Hal” or “halogen” when used in the context of the present invention refers to –F, –Cl, –Br or –I. Preferably, the halogen is –Cl or –Br, more preferably –Cl.

The term “OAc” refers in the context of the present invention to an acetate ion $^{-}O(O)C\text{-}CH_3$.

The term “$-(C_1\text{-}C_4)$alkyl” refers according to the invention to a straight chained or branched aliphatic alkyl residue having one to four carbon atoms, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or tert-butyl.

The present invention relates to a process for providing a compound of formula (IV), as defined above, comprising the step of: reacting a compound of formula (III), as defined above in the presence of a Ag(I) compound, a Cu(II) compound, and a compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$.



Compounds of formula (III), in which R^3 is an alkali metal, can be obtained by neutralizing a corresponding carboxylic acid using a suitable base. The base for neutralizing the corresponding carboxylic acid is not specifically limited and is preferably selected from alkali metal alkoxides, such as alkali metal (C_1-C_4)alkoxides. An especially preferred base is potassium tert-butoxide. The base is typically used in stoichiometric amounts. The resulting alkali metal carboxylate salts of formula (III) can be isolated or can be prepared in-situ.

The Ag(I) compound is according to the invention preferably selected from Ag_2CO_3, Ag(I) acetate (AgOAc), and Ag_2O, more preferably Ag_2CO_3. The Ag(I) compound is present in an amount of about 0.1 to about 1.0 molar equivalents per one molar equivalent of the compound of formula (III), more preferably about 0.25 to about 1.0 molar equivalents. Especially in case a co-oxidant is present, it is possible and preferable to use the Ag(I) compound in substoichiometric amounts. Thus, in a still further preferred embodiment, the Ag(I) compound is present in an amount of about 0.25 molar equivalents.

The Cu(II) compound is according to the invention preferably selected from Cu(II) acetate, and $CuBr_2$. More preferably the Cu(II) compound is Cu(II) acetate ($Cu(OAc)_2$). The Cu(II) compound is present in an amount of preferably about 0.1 to about 1.0 molar equivalents per one molar equivalent of the compound of formula (III), more preferably about 0.2 to about 1.0 molar equivalents, still more preferably in an amount of about 1.0 molar equivalent.

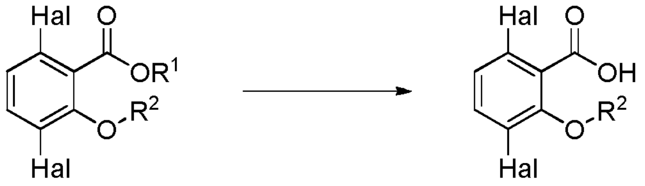
It is further preferred according to the present invention that the compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$ is $Si(OR^2)_4$. The compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$ is preferably present in an amount of about 1.0 to about 5.0 molar equivalents per one molar equivalent of the compound of formula (III), more preferably in an amount of about 5.0 molar equivalents.

As mentioned above, the step of reacting the compound of formula (III) according to the invention is preferably carried out in the additional presence of a co-oxidant as defined above. When a co-oxidant is used, substoichiometric amounts of the Ag(I) compound and/or Cu(II) compound can be used, which is preferable e.g. from the viewpoint of costs. The co-oxidant is preferably selected from molecular oxygen (O_2), benzoquinone, $K_2S_2O_8$, $Na_2S_2O_8$, and a peroxyacetic acid ester, such as peroxyacetic acid tert-butyl ester. More preferably, the co-oxidant is O_2.The co-oxidant is preferably present in an amount of about 0.8 to about 1.2 molar equivalents per one molar equivalent of the compound of formula (III), more preferably about 1.0 molar equivalent. When O_2 is used as the co-oxidant, which is preferred, it is provided at a pressure of about 100 kPa to about 200 kPa, more preferably about 101.3 kPa.

The above step of reacting the compound of formula (III) is carried preferably out at a temperature of about 100°C to about 160°C, more preferably about 115°C to about 150°C, still more preferably about 120°C to about 145°C.

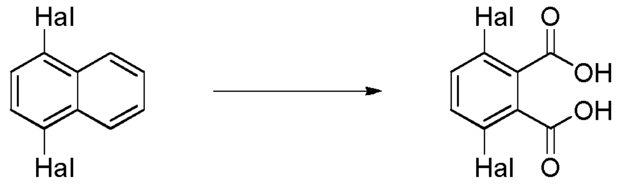
The step of reacting the compound of formula (III) is carried out in solution in an organic solvent. The organic solvent is not particularly limited as long as it does not interfere with the reaction. Preferred solvents include but are not limited to dioxane, 1,2-dichloroethane (DCE), acetonitrile, dimethylsulfoxide (DMSO), dimethylformamide (DMF), N-methylpyrrolidone (NMP), N,N-dimethylacetamide (DMA), or N,N-dimethylpropionamide (DMP), preferably DMF, DMA, or DMP, most preferably DMF.

Compounds of formula (IV), in which R^1 is $-(C_1-C_4)$alkyl, can be converted according to the invention to compounds of formula (IV), in which R^1 is hydrogen. The conversion can be carried out using a suitable base to obtain the corresponding carboxylic acid salts.



For example, alkali metal hydroxides such as NaOH may be employed here. Thus, a composition comprising alkali metal salts, such as sodium salts, are obtained. The alkali metal salt of a compound of formula (IV) is then acidified in aqueous solution using a suitable acid, such as H_2SO_4 or HCl, preferably HCl, to afford the compound of formula (IV), in which R^1 is hydrogen.

Carboxylic acids corresponding to compounds of formula (III), in which R^1 and R^3 are hydrogen (referred to as compounds of formula (IIIa), wherein Hal is as defined above), can be obtained from readily available materials in reaction steps suitable to be carried out on an industrial scale. For example, compounds of formula (IIIa) can be provided by oxidizing 1,4-dihalonaphthalenes of formula (II), wherein Hal is as defined above.

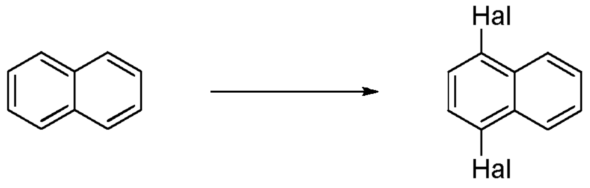


II **IIIa**

The above conversion may e.g. accomplished using HNO_3 as the oxidant. Compounds of formula (IIIa) can be converted to compounds of formula (III), in which R^1 is hydrogen and R^3 is an alkali metal, using a suitable base such as an alkali metal alkoxide as described above.

Thus, in a preferred embodiment, the present invention relates to a process as defined above, wherein the compound of formula (III) is obtained by oxidizing a compound of formula (II) and the resulting compound of formula (IIIa) is neutralized with about one molar equivalent of a suitable base such as an alkali metal alkoxide.

Furthermore, the compound of formula (II) in turn can be obtained by halogenating naphthalene (referred to as a compound of formula (I)).

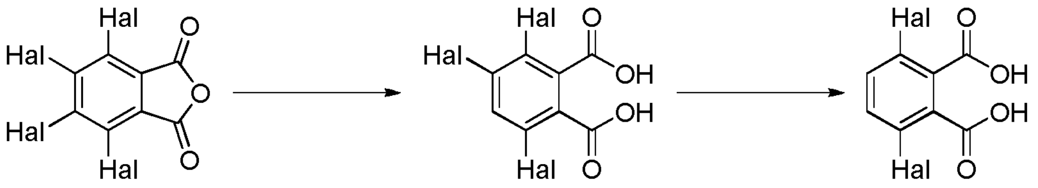


I **II**

The above reaction step can be carried out on an industrial scale, e.g. by aromatic free radical chlorination or bromination.

Thus, in a further preferred embodiment, the present invention relates to a process as defined above, wherein the compound of formula (II) is obtained by halogenating a compound of formula (I).

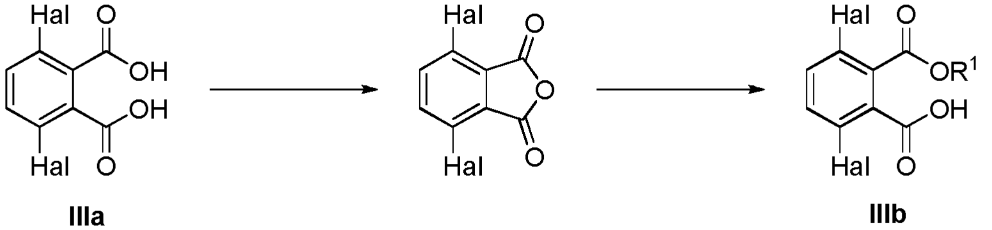
Alternatively, compounds of formula (IIIa) can be obtained by reductive dehalogenation from tetrahalophthalic acid anhydride using zinc powder as described in WO 00/05195.



IIIa

Thus, in a further preferred embodiment, the present invention relates to a process as defined above, wherein the compound of formula (III) is obtained by reductive dehalogenation of tetrahalophthalic acid, and the resulting compound of formula (IIIa) is neutralized with about one molar equivalent of a suitable base such as an alkali metal alkoxide.

Carboxylic acids corresponding to compounds of formula (III), in which R^1 is $-(C_1$-$C_4)$alkyl (referred to as a compound of formula (IIIb)), can be obtained by dehydrating the above compounds of formula (IIIa) to obtain 3,6-dihalophthalic acid anhydride. For example, compounds of formula (IIIa) may be combined in a suitable solvent such as toluene with catalytic amounts of acid (e.g. p-toluenesulfonic acid) under azeotropic removal of water to obtain 3,6-dihaolphthalic anhydride. Alternatively, the reaction may be carried out with acid chloride forming reagents such as $SOCl_2$ or $POCl_3$ in an inert solvent such as chlorinated solvents at increased temperature. According to a further alternative, the reaction may be accomplished in acetic acid at increased temperature. Subsequently, 3,6-dihalophthalic acid anhydride is reacted the with an alcohol of the formula HOR^1, wherein R^1 is $-(C_1\text{-}C_4)$alkyl, to obtain a compound of formula (IIIb), wherein Hal is as defined above and R^1 is $-(C_1\text{-}C_4)$alkyl. For example, 3,6-dihalophthalic acid anhydride may be dissolved in an alcohol of formula HOR^1 (e.g. methanol) together with a corresponding alkali metal $(C_1\text{-}C_4)$alkoxide (e.g. $NaOCH_3$) at increased temperature. Alternatively, 3,6-dihalophthalic acid anhydride may be dissolved in an alcohol of formula HOR^1 (e.g. methanol) together with catalytic amounts of acid (such as H_2SO_4 or HCl) at increased temperature.

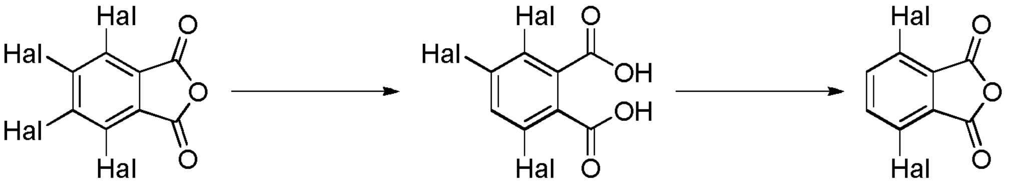


IIIa IIIb

Compounds of formula (IIIb) can be converted to compounds of formula (III), in which Hal is as defined above, R^1 is $-(C_1\text{-}C_4)$alkyl and R^3 is an alkali metal, using a suitable base such as an alkali metal alkoxide as described above.

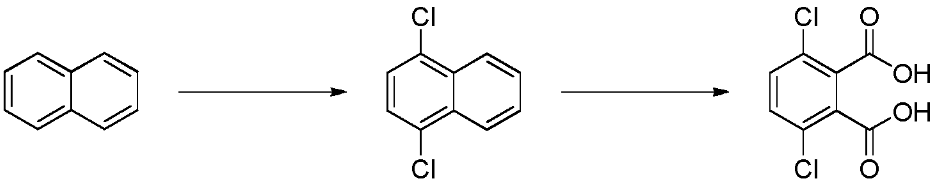
Thus, in a further preferred embodiment, the present invention relates to a process as defined above, wherein the compound of formula (III), in which R^1 is $-(C_1\text{-}C_4)$alkyl, is obtained by dehydrating a compound of formula (IIIa), reacting the resulting 3,6-dihalophthalic acid anhydride with an alcohol of the formula HOR^1, wherein R^1 is $-(C_1\text{-}C_4)$alkyl, and neutralizing the resulting compound of formula (IIIb) is neutralized with about one molar equivalent of a suitable base such as an alkali metal alkoxide.

In an alternative embodiment, 3,6-dihalophthalic acid can be obtained by reductive dehalogenation from tetrahalophthalic acid as described in WO 00/05194 under azeotropic removal of water.



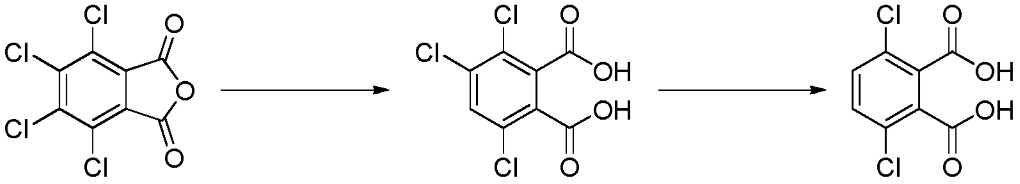
As described above, in preferred embodiments according to the present invention, Hal is –Cl, R^2 is methyl, and R^1 is hydrogen in the finally obtained product. Thus, the present invention provides in preferred embodiments an improved reaction sequence for obtaining dicamba.

In a first step of a possible reaction sequence, naphthalene is chlorinated for obtaining 1,4-dichloronaphthalene as described above. Subsequently, 1,4-dichloronaphthalene is oxidized using HNO_3 as described above to obtain 3,6-dichlorophthalic acid.

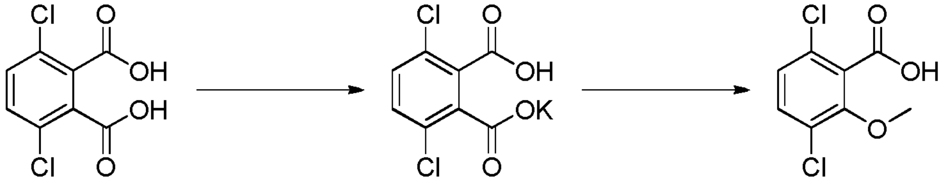


1,4-Dichloronaphthalene is a compound according to formula (II) of the present invention in which Hal is Cl. 3,6-Dichlorophthalic acid is a compound of formula (IIIa) according to the invention in which Hal is Cl.

Alternatively, 3,6-dichlorophthalic acid may be obtained by reductive dehalogenation of tertachlorophthalic acid. According to this embodiment, tetrachlorophthalic acid (1 equivalent) is combined in water with an alkali metal hydroxide such as NaOH (about 3.6 molar equivalents) and zinc powder (about 3.0 molar equivalents) at a temperature of about 70 to 80°C to afford trichlorophtahlic acid. Trichlorophthalic acid (1 equivalent) in turn can be converted to 3,6-dichlorophthalic acid by reacting with e.g. NaOH (about 6.0 molar equivalents) and zinc powder (about 5.8 molar equivalents) in water at a temperature of about 95 to 100°C.

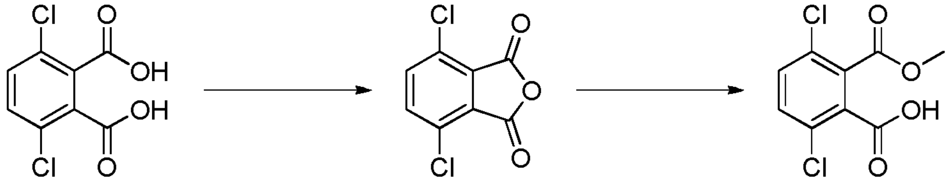


3,6-Dichlorophthalic acid can be partly neutralized using one molar equivalent of potassium tert-butoxide to provide potassium 2-carboxy-3,6-dichlorobenzoate which then is reacted according to the present invention using Ag_2CO_3, $Cu(OAc)_2$, $Si(OCH_3)_4$ and O_2 as described above to obtain after acidification dicamba.



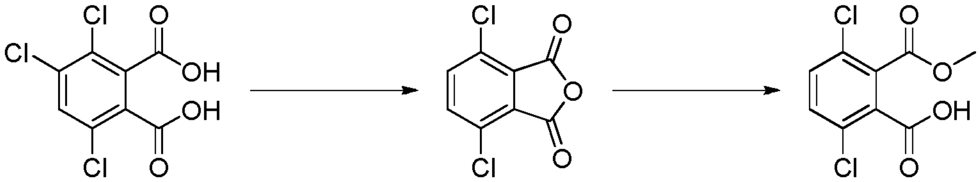
Potassium 2-carboxy-3,6-dichlorobenzoate is a compound of formula (III) according to the present invention in which R^1 is hydrogen, R^3 is potassium and Hal is Cl. Dicamba is a compound of formula (IV) of the invention.

Alternatively, 3,6-dichlorophthalic acid can be dehydrated and the resulting 3,6-dichlorophthalic acid anhydride can be reacted with methanol to provide 3,6-dichloro-2-(methoxycarbonyl)benzoic acid.

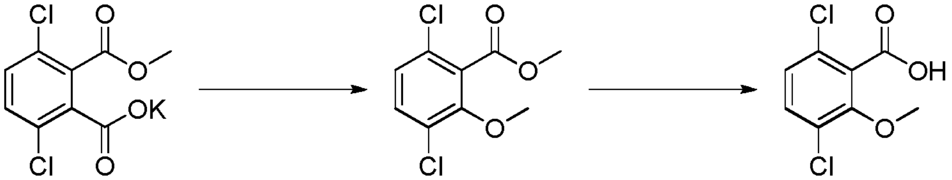


3,6-Dichloro-2-(methoxycarbonyl)benzoic acid is a compound of formula (IIIb) according to the present invention wherein R^1 is methyl.

Alternatively, 3,6-dichlorophthalic acid anhydride can be prepared by reductive dehalogenation from trichlorophthalic acid (which may be obtained as outlined above) under azeotropic removal of water, and subsequently can be reacted with methanol to provide 3,6-dichloro-2-(methoxycarbonyl)benzoic acid. For example, reacting trichlorophthalic acid to provide 3,6-dichlorophthalic acid anhydride can be accomplished with NaOH (about 6 molar equivalents), zinc powder (about 5.8 molar equivalents) in water at about 95 to 100°C, and subsequently adding HCl and azeotropic removal of water using toluene at about 110°C.



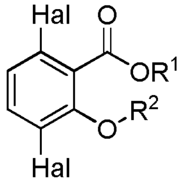
Subsequently, 3,6-dichloro-2-(methoxycarbonyl)benzoic acid is converted to potassium 3,6-dichloro-2-(methoxycarbonyl)benzoate using potassium tert-butoxide, and the resulting product is in turn is reacted according to the present invention using Ag_2CO_3, $Cu(OAc)_2$, $Si(OCH_3)_4$ and O_2 as described above to obtain after acidification methyl 3,6-dichloro-2-methoxybenzoate. Methyl 3,6-dichloro-2-methoxybenzoate is hydrolyzed as described above to obtain dicamba.



Potassium 3,6-dichloro-2-(methoxycarbonyl)benzoate is a compound of formula (III) according to the present invention in which Hal is Cl, R^1 is methyl and R^3 is potassium. Methyl 3,6-dichloro-2-methoxybenzoate is a compound of formula (IV) according to the invention in which Hal is Cl, R^1 is methyl and R^2 is methyl.

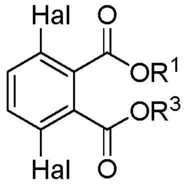
Claims

1. A process for providing a compound of formula (IV):



IV

wherein R^1 is hydrogen or $-(C_1-C_4)$alkyl, R^2 is $-(C_1-C_4)$alkyl, and each Hal is an independently selected halogen, the process comprising the step of:
Reacting a compound of formula (III)



III

wherein R^1 and Hal are defined as above, and R^3 is an alkali metal,
in the presence of a Ag(I) compound, a Cu(II) compound, and a compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$.

2. The process according to claim 1, wherein the step of reacting the compound of formula (III) is carried out in the further presence of a co-oxidant, preferably selected from O_2, benzoquinone, $K_2S_2O_8$, $Na_2S_2O_8$, and a peroxyacetic acid ester, more preferably O_2.

3. The process according to claim 1 or 2, wherein
   (a) the Ag(I) compound is selected from Ag_2CO_3, Ag(I) acetate and Ag_2O, and preferably is Ag_2CO_3; and/or
   (b) the Cu(II) compound is selected from Cu(II) acetate and $CuBr_2$, and preferably is Cu(II) acetate; and/or
   (c) the compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$ is $Si(OR^2)_4$.

4. The process according to any one of claims 1 to 3, wherein the

(a) the Ag(I) compound is present in an amount of about 0.1 to about 1.0 molar equivalents, preferably about 0.25 to about 1.0 molar equivalents, more preferably about 0.25 molar equivalents; and/or

(b) the Cu(II) compound is present in an amount of about 0.1 to about 1.0 molar equivalents, preferably about 0.2 to about 1.0 molar equivalents, more preferably about 1.0 molar equivalent; and/or

(c) the compound selected from $Si(OR^2)_4$ and $B(OR^2)_3$ is present in an amount of about 1.0 to about 5.0 molar equivalents, preferably about 5.0 molar equivalents; and/or

(d) the co-oxidant is present in an amount of about 0.8 to about 1.2 molar equivalents, preferably about 1.0 molar equivalent, or in, case the co-oxidant is O_2, it is provided at a pressure of about 100 kPa to about 200 kPa, preferably about 101.3 kPa,

based on one molar equivalent of the compound of formula (III).

5. The process according to any one of the preceding claims, wherein the step of reacting the compound of formula (III) is carried out at a temperature of about 100°C to about 160°C, preferably about 115°C to about 150°C, more preferably about 120°C to about 145°C.

6. The process according to any one of the preceding claims, wherein a compound of formula (IV), in which R^1 is $–(C_1\text{-}C_4)$alkyl, is reacted to obtain a compound of formula (IV), in which R^1 is hydrogen.

7. The process according to any one of the preceding claims, wherein

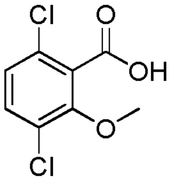
(a) Hal is selected from –F, –Cl, –Br and –I, preferably –Cl and –Br, more preferably –Cl; and/or

(b) R^1 is selected from hydrogen, methyl and ethyl, more preferably hydrogen; and/or

(c) R^2 is selected from methyl and ethyl, more preferably methyl; and/or

(d) R^3 is selected from lithium, sodium and potassium, more preferably sodium and potassium, most preferably potassium.

8. The process according to any one of the preceding claims, wherein the compound of formula (IV) is


Cl
O
OH
O
Cl

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/072990

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C67/32 C07C51/09 C07C69/92 C07C65/21
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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 161 611 A (KIM DONG-WHEE [US]) 17 July 1979 (1979-07-17) claim 1 columns 5-6; example 1 -----	1-8
A	US 3 013 054 A (RICHTER SIDNEY B) 12 December 1961 (1961-12-12) column 1, lines 25-35 columns 3-5; examples I-V ----- -/--	1-8

☒ 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

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"&" document member of the same patent family

Date of the actual completion of the international search 15 January 2015	Date of mailing of the international search report 27/01/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Guazzelli, Giuditta

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GARDNER L K ET AL: "Benzene production from decarboxylation of benzoic acid in the presence of ascorbic acid and a transition-metal catalyst", JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, AMERICAN CHEMICAL SOCIETY, US, vol. 41, no. 5, 1 May 1993 (1993-05-01), pages 693-695, XP003018352, ISSN: 0021-8561, DOI: 10.1021/JF00029A001 the whole document -----	1-8
A	WILLIAM G. TOLAND: "Oxidative Decarboxylation of Aromatic Acids to Isomeric Aryloxy Derivatives", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 83, no. 11, 1 June 1961 (1961-06-01), pages 2507-2512, XP055110606, ISSN: 0002-7863, DOI: 10.1021/ja01472a021 paragraph I; page 2510 - page 2511 -----	1-8

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/072990

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4161611	A	17-07-1979	NONE	
US 3013054	A	12-12-1961	NONE	