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(54) METHOD FOR PRODUCING FLUORINE-CONTAINING ORGANIC COMPOUND

(57) An object of the present disclosure is to provide a novel method for producing a fluorine-containing organic compound by electrolytic fluorination, and the like. The object can be achieved by a method for producing a fluorine-containing organic compound (1), comprising step A of subjecting an organic compound (2) to electrolytic fluorination in the presence of 0.2 M or more of a metal fluoride, and a fluoroalcohol.

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Description

Technical Field

[0001] The present disclosure relates to a method for producing a fluorine-containing organic compound.

Background Art

[0002] For example, electrolytic fluorination is a known method for producing fluorine-containing organic compounds. As a method of electrolytic fluorination, for example, the method described in Non-patent Literature 1 is known.

Citation List

Non-patent Literature

[0003] NPL 1: Sawamura et al., Angew. Chem. Int. Ed. 2012, 51, 4413

Summary of Invention

Technical Problem

[0004] An object of the present disclosure is to provide a novel method for producing a fluorine-containing organic compound by electrolytic fluorination, and the like.

Solution to Problem

Item 1.

[0005] A method for producing a fluorine-containing organic compound (1), comprising step A of subjecting an organic compound (2) to electrolytic fluorination in the presence of 0.2 M or more of a metal fluoride, and a fluoroalcohol.

Item 2.

[0006] The production method according to Item 1, wherein the fluorine-containing organic compound (1) is a fluorine-containing organic compound represented by formula (1):

$$R^1\text{-}(F)_n$$

wherein R^1 represents an organic group, and n represents an integer of 1 or more; and
the organic compound (2) is an organic compound represented by formula (2):
$R^1\text{-}(H)_n$, $R^1\text{-}(SR^{1a})_n$, or $R^1(=S)_{n/2}$
wherein R^1 and n are as defined above, and R^{1a} represents an organic group, provided that n/2 is an integer of 1 or more.

Item 3.

[0007] The production method according to Item 2, wherein the organic group is a (hetero)hydrocarbyl group optionally having one or more substituents.

Item 4.

[0008] The production method according to Item 2 or 3, wherein n is an integer of 2 or more.

Item 5.

[0009] The production method according to any one of Items 2 to 4, wherein R^1 is a polyether group.

Item 6.

[0010] The production method according to Item 1, wherein the fluorine-containing organic compound (1) is a ketone, an imine, a sulfide, an aromatic compound, a thiocarbonyl compound, or a polyether.

Item 7.

[0011] The production method according to any one of Items 1 to 6, wherein the metal fluoride is at least one metal fluoride selected from the group consisting of fluorides of metals belonging to Group 1 of the periodic table and fluorides of metals belonging to Group 2 of the periodic table.

Item 8.

[0012] The production method according to Item 7, wherein the metal fluoride is at least one metal fluoride selected from the group consisting of lithium fluoride, sodium fluoride, potassium fluoride, and cesium fluoride.

Item 9.

[0013] The production method according to any one of Items 1 to 8, wherein the fluoroalcohol is a C_{1-14} fluoroalcohol.

Item 10.

[0014] The production method according to Item 9, wherein the fluoroalcohol is a fluoroalcohol having a fluorine content within the range of 50 to 80 mass%.

Item 11.

[0015] The production method according to any one of Items 1 to 10, wherein step A is performed in the presence of an organic solvent, and the total volume of the fluoroalcohol and the organic solvent per mole of the organic compound (2) at the start of the electrolytic fluorination in step A is within the range of 0.1 to 100 L.

Item 12.

[0016] The production method according to any one of Items 1 to 11, wherein step A is performed in the presence of an organic solvent, and the volume ratio of the fluoroalcohol to the organic solvent at the start of the electrolytic fluorination in step A is 1/100 (v/v) or more.

Item 13.

[0017] The production method according to any one of Items 1 to 12, wherein the concentration of the metal fluoride (the concentration of the metal fluoride based on the entire liquid components in the system) in step A is within the range of 0.2 to 5 M.

Item 14.

[0018] The production method according to any one of Items 1 to 13, wherein the temperature of step A is 0°C or more.

Item 15.

[0019] A composition comprising 0.2 M or more of a metal fluoride, a fluoroalcohol, and an organic solvent.

Advantageous Effects of Invention

[0020] The present disclosure provides a novel method for producing a fluorine-containing organic compound, and the like.

Description of Embodiments

[0021] Although the details and form of the production method and the like according to the present disclosure are described below, it can be understood that various modifications in details and form may be made without departing from the spirit and scope of the claims.

[0022] It can be understood by a person skilled in the art in light of common technical knowledge that combinations of elements of the following embodiments and alternatives are possible.

Terms

[0023] Unless otherwise specified, the symbols and abbreviations in the present specification can be understood in the context of the present specification in the meanings commonly used in the technical field to which the production method and the like according to the present disclosure belong.

[0024] In the present specification, the terms "comprise" and "contain" are used with the intention of including the terms "consisting essentially of" and "consisting of."

[0025] In the present specification, room temperature can refer to a temperature within the range of 10 to 40°C.

[0026] In the present specification, the phrase "C_n-C_m" (n and m are each an integer of 1 or more, and $n<m$) indicates that the number of carbon atoms is n or more and m or less, as a person skilled in the art would generally understand.

[0027] In the present specification, unless otherwise specified, examples of "halo (group)" may include fluoro (group), chloro (group), bromo (group), and iodine (group).

[0028] In the present specification, unless otherwise specified, examples of "halogen (atom)" may include fluorine (atom), chlorine (atom), bromine (atom), and iodine (atom).

[0029] In the present specification, the term "organic group" refers to a group containing one or more carbon atoms (or a group formed by removing one hydrogen atom from an organic compound).

[0030] In the present specification, unless otherwise specified, the term "heteroatom" may refer to an atom other than hydrogen and carbon.

[0031] In the present specification, unless otherwise specified, examples of "heteroatom" include nitrogen atom, oxygen atom, and sulfur atom.

[0032] In the present specification, unless otherwise specified, the term "organic group" refers to a group containing one or more carbon atoms as its constituent atom.

[0033] In the present specification, unless otherwise specified, examples of "organic group" include (1) hydrocarbyl (optionally having one or more substituents) and (2) a group in which one or more heteroatoms are inserted into hydrocarbyl (optionally having one or more substituents) (which may be referred to as "heterohydrocarbyl" in the present specification).

[0034] Examples of the substituents include halo, nitro, cyano, oxo, thioxo, sulfo, sulfamoyl, sulfinamoyl, and sulfenamoyl.

[0035] In the present specification, unless otherwise specified, the term "hydrocarbyl (group)" refers to a group containing one or more carbon atoms and one or more hydrogen atoms as its constituent atoms.

[0036] Examples of "(1) hydrocarbyl" include an aliphatic hydrocarbyl group optionally substituted with one or more aromatic hydrocarbyl groups (e.g., a benzyl group), and an aromatic hydrocarbyl group optionally substituted with one or more aliphatic hydrocarbyl groups (aryl group in the narrow sense).

[0037] In the present specification, the term "(hetero)aryl group" includes an aryl group in the narrow sense and a heteroaryl group.

[0038] Examples of "(2) a group in which one or more heteroatoms are inserted into hydrocarbyl" (heterohydrocarbyl) include a 5- to 6-membered heteroaryl group, a group in which a benzene ring is fused to a 5- to 6-membered heteroaryl group, an alkoxy group, an ester group, an ether group, and a heterocyclic group.

[0039] In the present specification, unless otherwise specified, the term "aliphatic hydrocarbyl (group)" may be linear, branched, cyclic, or a combination thereof.

[0040] In the present specification, unless otherwise specified, the term "aliphatic hydrocarbyl (group)" may be saturated or unsaturated.

[0041] In the present specification, unless otherwise specified, examples of "aliphatic hydrocarbyl (group)" include an alkyl group, an alkenyl group, an alkynyl group, and a cycloalkyl group.

[0042] In the present specification, unless otherwise specified, examples of "alkyl (group)" include C_{1-10} linear or branched alkyl groups, such as methyl, ethyl, propyl (n-propyl and isopropyl), butyl (n-butyl, isobutyl, sec-butyl, and tert-butyl), pentyl, isopentyl, neopentyl, and hexyl.

[0043] In the present specification, unless otherwise specified, examples of "alkenyl (group)" include C_{1-10} linear or branched alkenyl groups (e.g., vinyl, 1-propenyl, isopropenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 2-ethyl-1-butenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 4-methyl-3-pentenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, and 5-hexenyl).

[0044] In the present specification, unless otherwise specified, examples of "alkynyl (group)" include C_{2-6} linear or branched alkynyl groups (e.g., ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-pentynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, and 5-hexynyl).

[0045] In the present specification, unless otherwise specified, examples of "cycloalkyl (group)" include C_{3-8} cycloalkyl groups (e.g., cyclopentyl, cyclohexyl, and cycloheptyl).

[0046] In the present specification, unless otherwise specified, examples of "aromatic hydrocarbyl (group) (aryl (group))" include phenyl, naphthyl, phenanthryl, anthryl, and pyrenyl.

[0047] In the present specification, unless otherwise specified, the term "aralkyl (group)" may refer to an alkyl group substituted with one aryl group, as is generally understood.

[0048] In the present specification, unless otherwise specified, the term "alkoxy (group)" is, for example, a group represented by RO- (wherein R is an alkyl group).

[0049] In the present specification, unless otherwise specified, the term "ester group" refers to an organic group having an ester bond (i.e., -C(=O)-O- or -O-C(=O)-). Examples of "ester group" include a group represented by formula: RCO_2-(wherein R is an alkyl group) and a group represented by formula: R^a-CO_2-R^b- (wherein R^a is an alkyl group, and R^b is an alkylene group).

[0050] In the present specification, unless otherwise specified, the term "ether group" refers to a group having an ether bond (-O-).

[0051] Examples of "ether group" include polyether groups.

[0052] Examples of polyether groups include a group represented by formula: R^a-$(O$-$R^b)_n$- (wherein R^a is an alkyl group, R^b, in each occurrence, is the same or different and represents an alkylene group, and n is an integer of 1 or more).

[0053] An alkylene group refers to a divalent group formed by removing one hydrogen atom from an alkyl group mentioned above.

[0054] Examples of "ether group" also include hydrocarbyl ether groups.

[0055] A hydrocarbyl ether group refers to a hydrocarbyl group having one or more ether bonds. The "hydrocarbyl group having one or more ether bonds" may be a hydrocarbyl group into which one or more ether bonds are inserted. Examples thereof include a benzyloxy group.

[0056] Examples of "hydrocarbyl group having one or more ether bonds" include an alkyl group having one or more ether bonds.

[0057] The "alkyl group having one or more ether bonds" may be an alkyl group into which one or more ether bonds are inserted. In the present specification, such a group may be referred to as "alkyl ether group"

[0058] In the present specification, unless otherwise specified, the term "acyl (group)" includes an alkanoyl group. In the present specification, unless otherwise specified, the term "alkanoyl (group)" is, for example, a group represented by RCO-(wherein R is an alkyl group).

[0059] In the present specification, examples of "5- to 6-membered heteroaryl (group)" include 5- to 6-membered heteroaryl groups having at least one heteroatom (e.g., one, two, or three heteroatoms) selected from the group consisting of oxygen, sulfur, and nitrogen as a ring-constituting atom, such as pyrrolyl (e.g., 1-pyrrolyl, 2-pyrrolyl, and 3-pyrrolyl), furyl (e.g., 2-furyl and 3-furyl), thienyl (e.g., 2-thienyl and 3-thienyl), pyrazolyl (e.g., 1-pyrazolyl, 3-pyrazolyl, and 4-pyrazolyl), imidazolyl (e.g., 1-imidazolyl, 2-imidazolyl, and 4-imidazolyl), isoxazolyl (e.g., 3-isoxazolyl, 4-isoxazolyl, and 5-isoxazolyl), oxazolyl (e.g., 2-oxazolyl, 4-oxazolyl, and 5-oxazolyl), isothiazolyl (e.g., 3-isothiazolyl, 4-isothiazolyl, and 5-isothiazolyl), thiazolyl (e.g., 2-thiazolyl, 4-thiazolyl, and 5-thiazolyl), triazolyl (e.g., 1,2,3-triazol-4-yl and 1,2,4-triazol-3-yl), oxadiazolyl (e.g., 1,2,4-oxadiazol-3-yl and 1,2,4-oxadiazol-5-yl), thiadiazolyl (e.g., 1,2,4-thiadiazol-3-yl and 1,2,4-thiadiazol-5-yl), tetrazolyl, pyridyl (e.g., 2-pyridyl, 3-pyridyl, and 4-pyridyl), pyridazinyl (e.g., 3-pyridazinyl and 4-pyridazinyl), pyrimidinyl (e.g., 2-pyrimidinyl, 4-pyrimidinyl, and 5-pyrimidinyl), and pyrazinyl.

Production Method

[0060] The production method according to one embodiment of the present disclosure is a method for producing a fluorine-containing organic compound (1), comprising step A of subjecting an organic compound (2) to electrolytic fluorination in the presence of 0.2 M or more of a metal fluoride, and a fluoroalcohol.

[0061] In the present disclosure, examples of the organic compound (2) as a reaction substrate include

(2-1) ketones (e.g., diketones such as 1,3-diketone, β-ketocarboxylic acids, and β-keto esters), and imines (e.g., Schiff bases and hydrazones),
(2-2) sulfides,
(2-3) aromatic compounds (e.g., aromatic hydrocarbons, phenylhydrazine derivatives, phenol derivatives, 2-naphthol derivatives, and aniline derivatives), and
(2-4) thiocarbonyl compounds.

[0062] In the present disclosure, fluorination of the organic compound means, in addition to substitution of a hydrogen atom by a fluorine atom, substitution (or replacement) of, for example, the following atom or group by a fluorine atom, as shown in the parentheses below: hydrogen atom (CH→CF) or hydrazino group ($C\text{-}NHNH_2 \rightarrow C\text{-}F$; $C{=}N\text{-}NH_2 \rightarrow CF_2$).

[0063] Examples of fluorination in the production method according to the present disclosure are described below. Examples of the fluorine-containing organic compound (1) obtained by the production method according to the present disclosure are also described below.

[0064] In the present disclosure, optionally having a substituent includes both cases where a substituent is contained (i.e., substituted) and not contained (i.e., unsubstituted). For example, an alkyl group optionally having a substituent includes an alkyl group (i.e., an unsubstituted alkyl group) and an alkyl group having a substituent (i.e., a substituted alkyl group).

(2-1) Fluorination of Ketones (Including Diketones, β-Ketocarboxylic Acids, and β-Keto Esters), and Imines such as Schiff Bases and Hydrazones

[0065] In the fluorination, for example, any of the following reactions (2-1-1) to (2-1-4) is performed.

(2-1-1) $R^2\text{-}C({=}X)\text{-}CH_2\text{-}C({=}X)\text{-}R^{2a} \rightarrow R^2\text{-}C({=}X)\text{-}CHF\text{-}C({=}X)\text{-}R^{2a}$ and/or $R^2\text{-}C({=}X)\text{-}CF_2\text{-}C({=}X)\text{-}R^{2a}$

(2-1-2) $H\text{-}C({=}X)\text{-}CH_2\text{-}C({=}X)\text{-}R^{2a} \rightarrow H\text{-}C({=}X)\text{-}CHF\text{-}C({=}X)\text{-}R^{2a}$ and/or $H\text{-}C({=}X)\text{-}CF_2\text{-}C({=}X)\text{-}R^{2a}$

(2-1-3) $R^2\text{-}C({=}N\text{-}NHR^{2b})\text{-}R^{2a} \rightarrow R^2\text{-}CF(\text{-}N{=}NR^{2b})\text{-}R^{2a}$ and/or $R^2\text{-}CF_2\text{-}R^{2a}$

(2-1-4) $H\text{-}C({=}N\text{-}NHR^{2b})\text{-}R^{2a} \rightarrow F_2C(\text{-}N{=}NR^{2b})\text{-}R^{2a}$ and/or $CF_3\text{-}R^{2a}$

wherein

X, in each occurrence, is the same or different and represents O or NR' (R' represents a hydrogen atom, an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl group optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, a heterocyclic group optionally having one or more substituents, an alkoxy group optionally having one or more substituents, an aryloxy group optionally having one or more substituents, an amino group, a monoalkylamino group optionally having one or more substituents, a dialkylamino group optionally having one or more substituents, an acyl group, or an acylamino group);

R^2 represents an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl group optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, a heterocyclic group optionally having one or more substituents, an alkoxy group optionally having one or more substituents, an aryloxy group optionally having one or more substituents, a monoalkylamino group optionally having one or more substituents, a dialkylamino group optionally having one or more substituents, an acyl group, or an acylamino group;

R^{2a} and R^{2b} are the same or different and each represents a hydrogen atom, an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl group optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, a heterocyclic group optionally having one or more substituents, an alkoxy group optionally having one or more substituents, an aryloxy group optionally having one or more substituents, a monoalkylamino group optionally having one or more substituents, a dialkylamino group optionally having one or more substituents, an acyl group, or an acylamino group; and R^2 and R^{2a} are optionally bonded to each other to form a cyclic structure.

[0066] Examples of the cyclic structure include 4- to 7-membered aliphatic rings optionally having one or more substituents; and the like.

[0067] R^2 is preferably an alkyl group, an aralkyl group, an aryl group, an alkenyl group, a heterocyclic group, an alkoxy group, an aryloxy group, or a monoalkylamino group. R', R^{2a}, and R^{2b} are each preferably a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkenyl group, a heterocyclic group, an alkoxy group, an aryloxy group, or a monoalkylamino group.

[0068] Examples of ketones include dialkyl ketones (e.g., acetone and methyl ethyl ketone), diketones (e.g., acetylacetone, acetoacetic acid, and acetoacetic acid esters), cycloalkanones (e.g., cyclohexanone), alkyl aryl ketones (e.g., acetophenone and propiophenone), diaryl ketones (e.g., benzophenone), 4-piperidone, 1-oxo-1,2-dihydronaphthalene, aryl(arylalkenyl)ketones (e.g., benzylideneacetophenone (chalcone)), aryl aralkyl ketones (e.g., deoxybenzoin), and ketals thereof, and the like.

[0069] Examples of imines such as Schiff bases and hydrazones include condensates of a ketone or an aldehyde with an appropriate primary amine or an appropriate hydrazine.

(2-2) Fluorination of Sulfides (Including Dithioacetals and Dithioketals)

[0070] In the fluorination, for example, a reaction in which one or two hydrogen atoms of methylene adjacent to a sulfur atom (or one hydrogen atom of -CHQ- (Q is an organic group)) are substituted by fluorine atom(s), or -SQ (Q is an organic group) is substituted by fluorine is performed. In the fluorination, for example, any one of the following reactions (2-2-1) to (2-2-7) is performed.

(2-2-1) $R^{3}\text{-}CHR^{3b}\text{-}S\text{-}R^{3a} \rightarrow R^{3}\text{-}CFR^{3b}\text{-}S\text{-}R^{3a}$

(2-2-2) $R^{3}\text{-}CO\text{-}CH_{2}\text{-}S\text{-}R^{3a} \rightarrow R^{3}\text{-}CO\text{-}CFH\text{-}S\text{-}R^{3a}$ and/or $R^{3}\text{-}CO\text{-}CF_{2}\text{-}S\text{-}R^{3a}$

(2-2-3) $R^{3}\text{-}CO\text{-}CHR^{3b}\text{-}S\text{-}R^{3a} \rightarrow R^{3}\text{-}CO\text{-}CFR^{3b}\text{-}S\text{-}R^{3a}$

(2-2-4) $R^{3c}R^{3d}C{=}C(SR^{3a})_{2} \rightarrow R^{3c}R^{3d}CH\text{-}CF_{2}\text{-}SR^{3a}$ and/or $R^{3c}R^{3d}CH\text{-}CF_{3}$

(2-2-5) $R^{3c}R^{3d}C(SR^{3a'})(SR^{3a''}) \rightarrow R^{3c}R^{3d}CF_{2}$

(2-2-6) $R^{3}\text{-}C(SR^{3a})(SR^{3a'})(SR^{3a''}) \rightarrow R^{3}\text{-}CF_{3}$

(2-2-7) $R^{3}\text{-}C(SR^{3a})(SR^{3a'})\text{-}S\text{-}R^{3e}\text{-}S\text{-}(SR^{3a'})(SR^{3a})\text{-}R^{3} \rightarrow R^{3}\text{-}CF_{3}$

wherein

R^{3a}, $R^{3a'}$, and $R^{3a''}$ are the same or different and each represents an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl group optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, or a heterocyclic group optionally having one or more substituents, or

R^{3a} and $R^{3a'}$, or $R^{3a'}$ and $R^{3a''}$ together represent a 4- to 7-membered aliphatic ring optionally having one or more substituents;

R^{3} and R^{3b} are the same or different and each represents an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl group optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, a heterocyclic group optionally having one or more substituents, an alkoxy group optionally having one or more substituents, an aryloxy group optionally having one or more substituents, an amino group, a monoalkylamino group optionally having one or more substituents, a dialkylamino group optionally having one or more substituents, an acyl group, an acylamino group, a cyano group, an alkylsulfinyl group optionally having one or more substituents, an aralkylsulfinyl group optionally having one or more substituents, an arylsulfinyl group optionally having one or more substituents, a cycloalkylsulfinyl group optionally having one or more substituents, a heterocycloalkylsulfinyl group optionally having one or more substituents, a sulfinyl group to which a heterocyclic group optionally having one or more substituents is bonded, an alkylsulfonyl group optionally having one or more substituents, an aralkylsulfonyl group optionally having one or more substituents, an arylsulfonyl group optionally having one or more substituents, a cycloalkylsulfonyl group optionally having one or more substituents, a heterocycloalkylsulfonyl group optionally having one or more substituents, or a sulfonyl group to which a heterocyclic group optionally having one or more substituents is bonded, or

R^{3} and R^{3b}, taken together with a carbon atom to which they are attached, optionally form a 4- to 8-membered ring via or not via a heteroatom (the ring is optionally substituted with at least one substituent selected from the group consisting of a halogen atom, an oxo group, an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cyano group, and an amino group); and R^{3c} and R^{3d}

are the same or different and each represents a hydrogen atom, an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, a heterocyclic group optionally having one or more substituents, an alkoxy group optionally having one or more substituents, an aryloxy group optionally having one or more substituents, an amino group, a monoalkylamino group optionally having one or more substituents, a dialkylamino group optionally having one or more substituents, an acyl group, an acylamino group, or a cyano group, or

R^{3c} and R^{3d}, taken together with an adjacent carbon atom, optionally form a saturated or unsaturated 4- to 7-membered aliphatic ring optionally having one or more substituents (the ring is optionally substituted with at least one substituent selected from the group consisting of a halogen atom, an oxo group, an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cyano group, and an amino group).

[0071] R^{3a}, $R^{3a'}$, and $R^{3a''}$ are each preferably an alkyl group, an aryl group, or an alkenyl group. R^3, R^{3b}, R^{3c}, and R^{3d} are each preferably an alkyl group, an aralkyl group, an aryl group, an alkenyl group, a heterocyclic group, an alkoxy group, an aryloxy group, an amino group, or a cyano group.

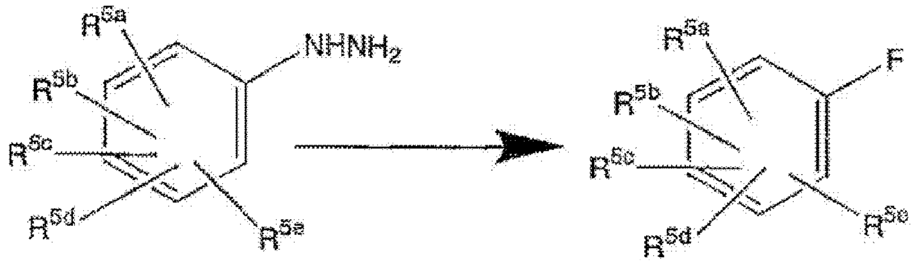
[0072] Examples of sulfides include dialkyl sulfides (e.g., methyl ethyl sulfide), alkyl aralkyl sulfides (e.g., methyl benzyl sulfide), 2-arylthioacetic acid esters (e.g., 2-phenylthioacetic acid ester), alkyl(arylthio)ketones (e.g., 2-(phenylthio)acetophenone), alkyl(alkylthio)ketones (e.g., 2-(methylthio)acetophenone), 2-aryloxy-2-(arylthio)acetonitrile (e.g., 2-phenoxy-2-(phenylthio)acetonitrile), bis(alkylthio)alkylarenes (e.g., bis(methylthio)methylbenzene), bis(arylthio)diarylmethanes (e.g., bis(phenylthio)diphenylmethane), 1,3-dithianes having one or more substituents at the 2-position (e.g., 2-octyl-1,3-dithiane), 1,3-dithiolanes having one or more substituents at the 2-position (e.g., 2-phenyl-2-trifluoromethyl-1,3-dithiolane and 2,2-diphenyl-1,3-dithiolane), tris(alkylthio)alkanes (e.g., tris(ethylthio)hexane), tris(alkylthio)alkylarenes (e.g., α,α,α-tris(methylthio)toluene), and the like.

(2-3) Fluorination of Aromatic Compounds

[0073] In the fluorination, for example, any of the following reactions (2-3-1) to (2-3-5) is performed. In reactions (2-3-1) to (2-3-4), one or more fluorine substituents are introduced into the aromatic moiety. As shown in reaction (2-3-2) or (2-3-4), fluorination of the aromatic ring of a phenol derivative or an aniline derivative can be carried out by fluorinating it and then reducing it with a reducing agent, such as zinc dust, to obtain the desired fluorinated compound.

(2-3-1) Fluorination of Phenylhydrazine Derivatives

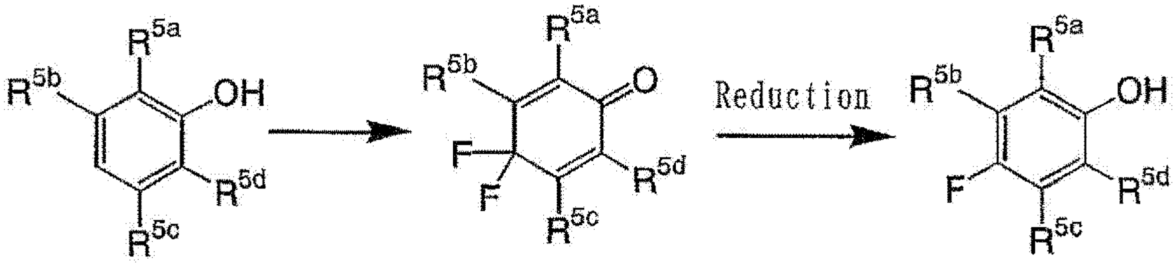
[0074] In the fluorination, a phenylhydrazine residue ($-NHNH_2$) optionally having one or more substituents can be replaced by a fluorine atom.

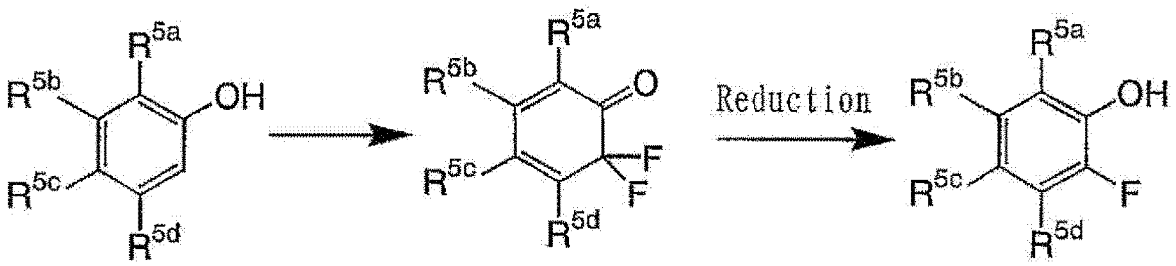


wherein R^{5a}, R^{5b}, R^{5c}, R^{5d}, and R^{5e} are the same or different and each represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a nitro group, a cyano group, a halogen atom, an alkanoyl group, an arylcarbonyl group, an amino group, a monoalkylamino group, a dialkylamino group, an alkanoylamino group, an arylcarbonylamino group, or an alkylthio group.

(2-3-2) Fluorination of Phenol Derivatives

[0075] In the fluorination, a phenol derivative forms, for example, the difluorinated quinonoid structure shown below, followed by reduction, thereby producing a phenol derivative having fluorine introduced at a position ortho or para to the hydroxyl group.





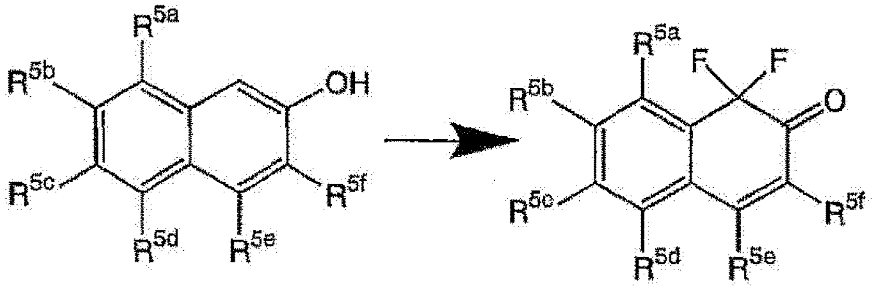
wherein R^{5a}, R^{5b}, R^{5c}, and R^{5d} are the same or different and each represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a nitro group, a cyano group, a halogen atom, an alkanoyl group, an arylcarbonyl group, an amino group, a monoalkylamino group, a dialkylamino group, an alkanoylamino group, an arylcarbonylamino group, or an alkylthio group.

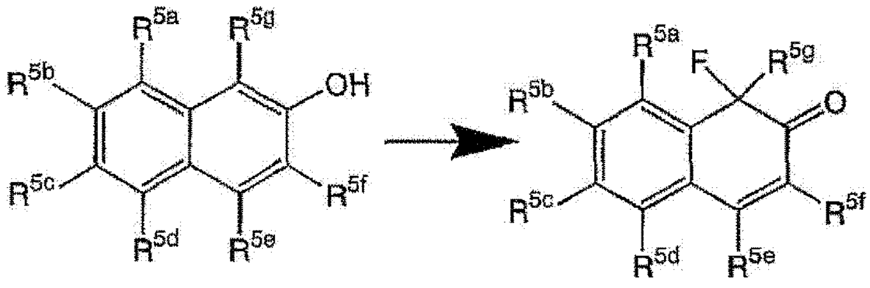
[0076] When a starting material substituted at all of the ortho- and para-positions is used, a fluorine atom is introduced into an ortho-position or a para-position, thereby forming a compound having a fluorinated quinonoid structure.

[0077] In the above example, phenol optionally having one or more substituents is used as a phenol derivative; however, it is also possible to introduce a fluorine atom into benzene-based aromatic compounds or condensed polycyclic hydrocarbons that have an electron-donating group, such as a hydroxyl group or an alkoxy group and are further optionally substituted.

(2-3-3) Fluorination of 2-Naphthol Derivatives

[0078] In the fluorination, mono- or di-fluorination at the 1-position of naphthol can be performed.



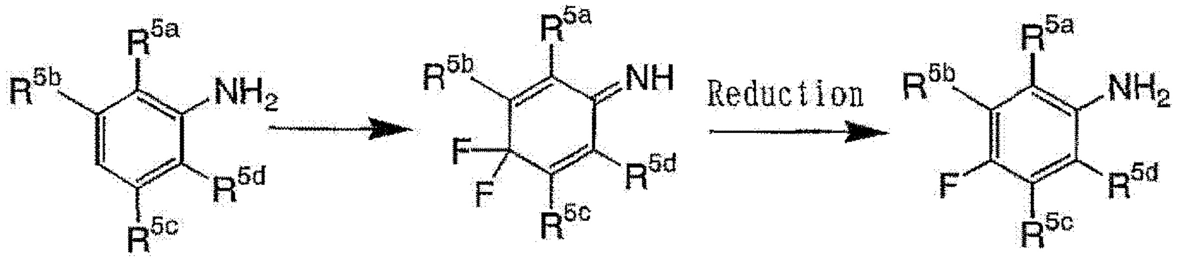


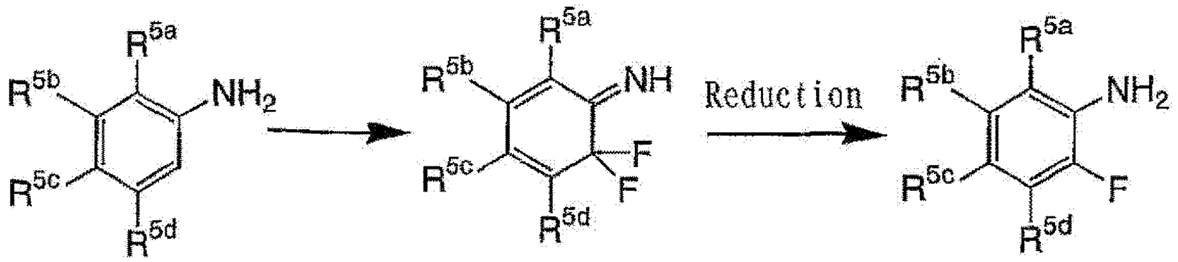
wherein

R^{5a}, R^{5b}, R^{5c}, R^{5d}, R^{5e}, and R^{5f} are the same or different and each represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a nitro group, a cyano group, a halogen atom, an alkanoyl group, an arylcarbonyl group, an amino group, a monoalkylamino group, a dialkylamino group, an alkanoylamino group, an arylcarbonylamino group, or an alkylthio group; and
R^{5g} represents an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a nitro group, a cyano group, a halogen atom, an alkanoyl group, an arylcarbonyl group, an amino group, a monoalkylamino group, a dialkylamino group, an alkanoylamino group, an arylcarbonylamino group, or an alkylthio group.

(2-3-4) Fluorination of Aniline Derivatives

[0079] In the fluorination, similar to a phenol derivative, an aniline derivative forms, for example, the difluorinated quinonoid structure shown below, followed by reduction, thereby producing an aniline derivative having fluorine introduced at an ortho-positon or the para-position.





wherein R^{5a}, R^{5b}, R^{5c}, and R^{5d} are the same or different and each represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a nitro group, a cyano group, a halogen atom, an alkanoyl group, an arylcarbonyl group, an amino group, a monoalkylamino group, a dialkylamino group, an alkanoylamino group, an arylcarbonylamino group, or an alkylthio group.

[0080] In the above example, aniline optionally having one or more substituents is used as an aniline derivative; however, it is also possible to introduce a fluorine atom into an aromatic ring when naphthylamine optionally having one or more substituents is used.

(2-3-5) Fluorination of (Hetero)arylmethyl Moiety-Containing Compounds

[0081] As shown in the following formula, the carbon at the 1-position of the (hetero)arylmethyl moiety in a (hetero)arylmethyl moiety-containing compound (e.g., the benzylic position in a benzyl moiety-containing compound) can be subjected to mono- or di-fluorination.

$$\text{Ar-CHR'-R} \rightarrow \text{Ar-CFR'-R}$$

and/or

$$\text{Ar-CF}_2\text{-R}$$

wherein

Ar represents a (hetero)aryl group (e.g., a 5- to 6-membered aromatic ring group) optionally having one or more substituents;

R represents an alkyl group, -C(=O)-OR^s, -NR^s, -C(=O)-R^s, -C(=O)-R^s, -CN, or a (hetero)aryl group (e.g., a 5- to 6-membered aromatic ring group) optionally having one or more substituents;

R' represents -H, an alkyl group, -C(=O)-OR^s, -NR^s, -C(=O)-R^s, -C(=O)-R^s, -CN, or a (hetero)aryl group (e.g., a 5- to 6-membered aromatic ring group) optionally having one or more substituents; and

R^s, in each occurrence, is the same or different and represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a nitro group, a cyano group, a halogen atom, an alkanoyl group, an arylcarbonyl group, an amino group, a monoalkylamino group, a dialkylamino group, an alkanoylamino group, an arylcarbonylamino group, or an alkylthio group.

[0082] The 5- to 6-membered aromatic ring group may be a phenyl group or a 5- to 6-membered heteroaryl group.

[0083] Examples of (hetero)arylmethyl moiety-containing compounds include triarylmethanes (e.g., triphenylmethane), aryldialkylmethanes (e.g., 4-bromocumene), and arylacetic acid esters (e.g., ethyl (4-methoxyphenyl)acetate).

(2-4) Fluorination of Thiocarbonyl Compounds (Including Thioketone, Thioester, Thiocarbonic Acid Ester, Thioamide, Dithiocarboxylic Acid Ester, and Dithiocarbamate)

[0084] In the fluorination, for example, the following reaction (2-4-1) or (2-4-2) is performed:

(2-4-1) $R^6\text{-C(=S)-}R^{6a} \rightarrow R^6\text{-CF}_2\text{-}R^{6a}$

(2-4-2) $R^6\text{-C(=S)-SR}^{6b} \rightarrow R^6\text{-CF}_2\text{-SR}^{6b}$ and/or $R^6\text{-CF}_3$

wherein

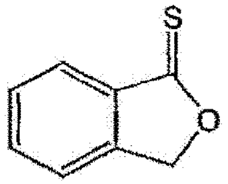
R^6 and R^{6a} are the same or different and each represents a hydrogen atom, an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl group optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, a heterocyclic group optionally having one or more substituents, an alkoxy group optionally having one or more substituents, an aryloxy group optionally having one or more substituents, a monoalkylamino group optionally having one or more substituents, a dialkylamino group optionally having one or more substituents, an acyl group, or an acylamino group;

R^6 and R^{6a} are optionally bonded to each other to form a cyclic structure; and

R^{6b} represents an alkyl group optionally having one or more substituents, an aralkyl group optionally having one or more substituents, an aryl group optionally having one or more substituents, an alkenyl group optionally having one or more substituents, a cycloalkyl group optionally having one or more substituents, a heterocycloalkyl group optionally having one or more substituents, or a heterocyclic group optionally having one or more substituents.

[0085] R^6, R^{6a}, and R^{6b} are each preferably an alkyl group, an aralkyl group, an aryl group, or an alkenyl group.

[0086] Examples of thiocarbonyl compounds include O-aryl S-alkyl dithiocarbonates (e.g., O-(4-isopropylphenyl)S-methyl dithiocarbonate and O-(4-bromophenyl)S-methyl) dithiocarbonate), ((alkylthio)carbonothioyl)oxybenzoic acid esters (e.g., ethyl 4-(((methylthio)carbonothioyl)oxy)benzoate), O-alkyl S-alkyl dithiocarbonates (e.g., O-decyl S-methyl dithiocarbonate), O-aralkyl S-alkyl dithiocarbonates (e.g., O-(3-phenylpropyl)S-methyl) dithiocarbonate), O-alkyl cycloalkanecarbothioates (e.g., O-methyl cyclohexanecarbothioate), O-alkyl heteroarenecarbothioates (e.g., O-propyl 1-piperidinecarbothioate), dithiobenzoic acid esters (e.g., methyl dithiobenzoate), diarylthioketones (e.g., thiobenzophenone), thiobenzoic acid esters (e.g., O-phenyl thiobenzoate), N,N-dialkylarylthioamides (e.g., N,N-dimethylphenylthioamide), dithiocarboxylic acid esters (e.g., ethyl 3-quinolinedithiocarboxylate), fluoroalkanecarbothioylarenes (e.g., trifluoromethanecarbothioylnaphthalene), N-alkyl-N-arylfluoroalkanethioamides (e.g., N-methyl-N-phenyltrifluoromethanethioamide), N-aralkyl-N-arylfluoroalkane thioamides (e.g., N-benzyl-N-phenylheptafluoropropanethioamide), O-cycloalkyl S-alkyl dithiocarbonates (e.g., O-(4'-pentyl-[1,1'-bi(cyclohexane)]-4-yl)S-methyl) dithiocarbonate),



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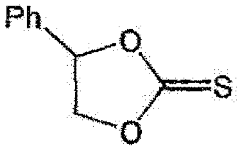

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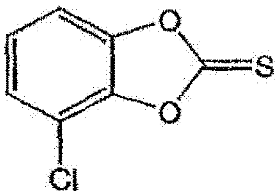
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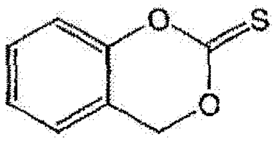

, and the like.

(2-5) Fluorination of Polyethers

[0087] In the fluorination, for example, hydrogen atom(s) attached to carbon atom(s) adjacent to the oxygen atom constituting an ether bond can be replaced by fluorine atom(s); however, the fluorination is not limited thereto. The number of fluorine atoms introduced in the fluorination is not particularly limited, and is, for example, one.

[0088] The polyether is not particularly limited and is, for example, a compound represented by formula (1A):

$$R^{7a}\text{-}(O\text{-}R^{7b})_p\text{-}O\text{-}R^{7c}$$

wherein

R^{7a} and R^{7c} are the same or different and each represents an organic group;
R^{7b} represents an alkylene group; and
p is 0 or an integer of 1 or more.

[0089] R^{7a} and R^{7c} are each preferably an alkyl group, an alkenyl group, an aryl group, or an aralkyl group. R^{7b} is preferably a C_{2-4} alkylene group.

[0090] p may be, for example, 50 or less, 40 or less, 30 or less, or 20 or less.

[0091] Examples of the compound represented by formula (1A) include ethylene glycol di-C_{1-4} alkyl ethers (e.g., monoglyme), polyethylene glycol di-C_{1-4} alkyl ethers (e.g., diglyme and triglyme), and the like.

[0092] In a preferred example of one embodiment, the fluorine-containing organic compound (1) is a fluorine-containing organic compound represented by formula (1):

$$R^1\text{-}(F)_n$$

wherein

R^1 represents an organic group; and
n represents an integer of 1 or more; and
the organic compound (2) is an organic compound represented by formula (2):
$R^1\text{-}(H)_n$, $R^1\text{-}(SR^{1a})_n$, $R^1\text{-}(NH\text{-}NH_2)_n$, $R^1\text{-}(N{=}NR^{1b})_n$, $R^1({=}N\text{-}NHR^{1c})_{n/2}$, or $R^1({=}S)_{n/2}$
wherein

R^1 and n are as defined above; and
R^{1a} to R^{1c} are the same or different and each is an organic group. When formula (2) is $R^1({=}N\text{-}NHR^{1c})_{n/2}$ or $R^1({=}S)_{n/2}$, n/2 is an integer of 1 or more, that is, n is a multiple of 2.

[0093] The organic group represented by each of R^1 and R^{1a} may contain one or more fluoro groups within it.

[0094] The organic group is preferably a (hetero)hydrocarbyl group optionally having one or more substituents.

[0095] In the production method according to the present disclosure, one or more fluorine atoms, preferably two or more fluorine atoms, are introduced into the organic compound (2), which is a substrate. In relation to this, in formula (1) and formula (2), n is preferably an integer of 2 or more. n is an integer less than or equal to the maximum number of possible substitutions in the organic compound (2). When n is an integer of 2 or more, the organic group represented by R^1 is an n-valent group formed by removing n-1 hydrogen atom(s) from a monovalent group described in the "Terms" section.

[0096] In the production method according to the present disclosure, for example, a desired compound into which one fluorine atom is introduced and a desired compound into which two fluorine atoms are introduced can both be obtained.

[0097] In one embodiment, formula (2) is R^1-H, wherein R^1 is preferably a triarylmethane residue (or a triarylmethyl group).

[0098] In one embodiment, formula (2) is R^1-H, wherein R^1 is preferably a polyether group.

[0099] In one embodiment, formula (2) is $R^1-(H)_2$, wherein R^1 is preferably

$$>C (C (=O)Q^1) (C (=O)Q^2)$$

wherein Q^1 and Q^2 are the same or different and each is a hydrogen atom, a hydroxyl group, or an organic group (e.g., an alkyl group, an alkenyl group, an aryl group, or an aralkyl group) or

$$>C (CO_2Q^3) (SQ^4)$$

wherein Q^3 and Q^4 are the same or different and each is a hydrogen atom or an organic group (e.g., an alkyl group, an alkenyl group, an aryl group, or an aralkyl group).

[0100] In one embodiment, formula (2) is $R^1-(SR^{1a})_2$, wherein R^1 is preferably

$$>CQ^5Q^6$$

wherein Q^5 and Q^6 are the same or different and each is an organic group (e.g., an alkyl group, an alkenyl group, an aryl group, or an aralkyl group), and

R^{1a} is preferably independently, in each occurrence, an organic group (e.g., an alkyl group, an alkenyl group, an aryl group, or an aralkyl group), or R^{1a} may be bonded to each other to form a ring structure.

[0101] In one embodiment, formula (2) is R^1=S, wherein R^1 is preferably

$$=CQ^7Q^8$$

wherein Q^7 and Q^8 are the same or different and each is an organic group (e.g., an alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, or an aralkyloxy group).

[0102] In one embodiment, formula (2) is $R^1-NH-NH_2$, wherein R^1 is preferably an alkyl group, an alkenyl group, an aryl group, or an aralkyl group.

[0103] In one embodiment, formula (2) is $R^1-N=NR^{1b}$, wherein R^1 is preferably an alkyl group, an alkenyl group, an aryl group, or an aralkyl group; and R^{1b} is preferably an alkyl group, an alkenyl group, an aryl group, or an aralkyl group.

[0104] In one embodiment, formula (2) is $R^1=N-NHR^{1c}$, wherein R^1 is preferably

$$=CQ^9Q^{10}$$

wherein Q^9 and Q^{10} are the same or different and each is an organic group (e.g., an alkyl group, an alkenyl group, an aryl group, or an aralkyl group).

[0105] The metal fluoride can function as a supporting salt (supporting electrolyte) in step A.

[0106] The metal fluoride is preferably at least one metal fluoride selected from the group consisting of fluorides of metals belonging to Group 1 of the periodic table and fluorides of metals belonging to Group 2 of the periodic table; and more preferably at least one metal fluoride selected from the group consisting of lithium fluoride, sodium fluoride, potassium fluoride, rubidium fluoride, cesium fluoride, and calcium fluoride.

[0107] The fluoroalcohol can function as an electrolytic solution in step A.

[0108] The fluoroalcohol is preferably a C_{1-14} fluoroalcohol.

[0109] The fluoroalcohol is preferably a fluoroalcohol represented by $RfCH_2OH$ or Rf_2CHOH, wherein Rf independently represents, in each occurrence, a C_{1-6} perfluoroalkyl group.

[0110] Specific examples of the fluoroalcohol include 2,2,3,3-tetrafluoro-1-propanol, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,3,3,3-pentafluoro-1-propanol. Preferred examples of the fluoroalcohol include 1,1,1,3,3,3-hexafluoro-2-propanol and 2,2,3,3,3-pentafluoro-1-propanol.

[0111] The fluoroalcohol is preferably a fluoroalcohol having a fluorine content of 50 mass% or more, more preferably a fluoroalcohol having a fluorine content of 55 mass% or more, and even more preferably a fluoroalcohol having a fluorine content of 60 mass% or more.

[0112] The fluoroalcohol is preferably a fluoroalcohol having a fluorine content of 80 mass% or less, more preferably a fluoroalcohol having a fluorine content of 75 mass% or less, and even more preferably a fluoroalcohol having a fluorine content of 70 mass% or less.

[0113] The fluoroalcohol is preferably a fluoroalcohol having a fluorine content within the range of 50 to 80 mass%, more preferably a fluoroalcohol having a fluorine content within the range of 55 to 75 mass%, and even more preferably a fluoroalcohol having a fluorine content within the range of 60 to 70 mass%.

[0114] The fluorine content (mass%) means the percentage of the mass of fluorine in one molecule of a fluoroalcohol.

[0115] The reaction of step A can be performed in the presence or absence of an organic solvent. Specific examples of the organic solvent are described later.

[0116] Preferably, step A is performed in the presence of an organic solvent.

[0117] The total volume of the fluoroalcohol and the organic solvent per mole of the organic compound (2) at the start of the electrolytic fluorination in step A is preferably 0.1 L or more, more preferably 1 L or more, and even more preferably 2 L or more.

[0118] The total volume of the fluoroalcohol and the organic solvent per mole of the organic compound (2) at the start of the electrolytic fluorination in step A is preferably 100 L or less, more preferably 50 L or less, and even more preferably 30 L or less.

[0119] The total volume of the fluoroalcohol and the organic solvent per mole of the organic compound (2) at the start of the electrolytic fluorination in step A is preferably within the range of 0.1 to 100 L, more preferably within the range of 1 to 50 L, and even more preferably within the range of 1 to 30 L.

[0120] When step A is performed in the presence of an organic solvent, the volume ratio of the fluoroalcohol to the organic solvent at the start of the electrolytic fluorination in step A is preferably 1/100 (v/v) or more, more preferably within the range of 0.2 to 2 (v/v), and even more preferably within the range of 0.5 to 1 (v/v).

[0121] The concentration of the metal fluoride (the concentration of the metal fluoride based on the entire liquid components in the system) in step A is preferably 0.2 M (mol/L) or more, more preferably within the range of 0.2 to 5 M (mol/L), even more preferably within the range of 0.2 to 2 M (mol/L), and still even more preferably within the range of 0.2 to 1 M (mol/L).

[0122] The lower limit of the temperature of step A may be preferably 0°C, more preferably 5°C, and even more preferably 10°C.

[0123] The upper limit of the temperature of step A may be preferably 150°C, more preferably 120°C, and even more preferably 100°C.

[0124] The temperature of step A is preferably within the range of 0 to 150°C, more preferably within the range of 0 to 120°C, and even more preferably within the range of 0 to 100°C.

[0125] In the above temperatures, the lower the upper limit of the temperature in step A, the more likely it is that side reactions can be suppressed. The higher the lower limit of the temperature in step A, the more likely it is that the progress of the desired reaction is promoted.

[0126] Step A can be performed at room temperature.

[0127] Step A can be performed in an atmosphere of air, an inert gas (e.g., nitrogen or argon), or a combination thereof.

[0128] The lower limit of the reaction time of step A may be preferably 0.5 hours, and more preferably 1 hour.

[0129] The upper limit of the reaction time of step A may be preferably 72 hours, more preferably 48 hours, and even more preferably 24 hours.

[0130] The reaction time of step A may be preferably within the range of 0.5 to 72 hours, more preferably within the range of 1 to 48 hours, and even more preferably within the range of 1 to 24 hours.

[0131] The shorter the upper limit of the reaction time of step A, the more likely it is that side reactions can be suppressed.

[0132] The longer the lower limit of the reaction time of step A, the more likely it is that the progress of the desired reaction is promoted.

[0133] As mentioned above, this reaction can be performed in the presence or absence of an organic solvent.

[0134] In the present specification, examples of organic solvents include

(1) alcohol solvents (e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, pentanol, hexanol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, trimethylene glycol, and hexanetriol);

(2) non-aromatic hydrocarbon solvents (e.g., pentane, hexane, heptane, octane, cyclohexane, decahydronaphthalene, n-decane, isododecane, and tridecane);

(3) aromatic hydrocarbon solvents (e.g., benzene, toluene, xylene, tetralin, veratrole, ethylbenzene, diethylbenzene, naphthalene, methylnaphthalene, anisole, mesitylene, indene, diphenyl sulfide);

(4) ketone solvents (e.g., acetone, methyl ethyl ketone, diethyl ketone, hexanone, methyl isobutyl ketone, heptanone, diisobutyl ketone, acetonylacetone, methylhexanone, acetophenone, cyclohexanone, diacetone alcohol, propiophenone, and isophorone);

(5) halogenated hydrocarbon solvents (e.g., dichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, chloroform, and chlorobenzene);

(6) ether solvents (e.g., diethyl ether, tetrahydrofuran (THF), diisopropyl ether, methyl-t-butyl ether (MTBE), dioxane, dimethoxyethane, diglyme, triglyme, tetraglyme, anisole, phenetole, 1,1-dimethoxycyclohexane, diisoamyl ether,

and cyclopentyl methyl ether (CPME));
(7) ester solvents (e.g., ethyl acetate, isopropyl acetate, butyl acetate, diethyl malonate, 3-methoxy-3-methylbutyl acetate, γ-butyrolactone, and α-acetyl-γ-butyrolactone);
(8) nitrile solvents (e.g., acetonitrile, propionitrile, and benzonitrile);
(9) sulfoxide solvents (e.g., dimethyl sulfoxide and sulfolane);
(10) amide solvents (e.g., N,N-dimethylformamide (DMF), N,N-dimethylacetamide, N-methylpyrrolidone (NMP), 1,3-dimethyl-2-imidazolidinone (DMI), N,N-dimethylacrylamide, N,N-dimethylacetamide (DMA), N,N-diethylformamide, and N,N-diethylacetamide);
(11) nitro solvents (e.g., nitromethane, nitroethane, nitrobenzene, 4-nitrophenetole, and o-nitrotoluene); and
(12) carbonate solvents (e.g., dimethyl carbonate, diethyl carbonate, dibutyl carbonate, ethylene carbonate, and propylene carbonate).

[0135] Particularly preferred solvents are inert solvents, such as aprotic solvents. Examples thereof include nitrile solvents (e.g., acetonitrile and propionitrile) and nitro solvents (e.g., nitromethane and nitroethane).

[0136] These solvents may be used singly or in a combination of two or more.

[0137] The electrolytic cell used in the electrolytic fluorination may be, for example, a diaphragm-free or diaphragm-type electrolytic cell, and a diaphragm-free electrolytic cell can be preferably used.

[0138] The electrolysis method may be, for example, constant-current electrolysis or controlled-potential electrolysis, and constant-current electrolysis can be preferably used.

[0139] Examples of usable electrodes include platinum electrodes, carbon electrodes, boron-doped diamond (BDD) electrodes, glassy carbon electrodes, silver electrodes, copper electrodes, and the like. Platinum electrodes can be preferably used.

[0140] According to the production method of the present disclosure, the starting material conversion can preferably be 10% or more, more preferably 30% or more, and even more preferably 50% or more.

[0141] According to the production method of the present disclosure, the yield of the desired compound in which one or more fluorine atoms are introduced can be preferably 50% or more, more preferably 60% or more, even more preferably 70% or more, and still even more preferably 80% or more.

[0142] According to the production method of the present disclosure, the yield of the desired compound in which two or more fluorine atoms are introduced can be preferably 10% or more, more preferably 15% or more, even more preferably 20% or more, and still even more preferably 25% or more.

Composition

[0143] The composition according to one embodiment of the present disclosure comprises 0.2 M or more of a metal fluoride, a fluoroalcohol, and an organic solvent.

[0144] The metal fluoride in a concentration of 0.2 M or more, the fluoroalcohol, and the organic solvent contained in the composition may be the same as those in the production method according to the present disclosure.

[0145] Thus, a person skilled in the art can understand the details of the composition and specific embodiments thereof based on the description of the production method according to the present disclosure.

Examples

[0146] The present disclosure is described below in more detail with reference to Examples; however, the present disclosure is not limited to these Examples.

Example 1

[0147] 2,2,2-Trifluoroethanol (2 mL), acetonitrile (8 mL), cesium fluoride (608 mg), and triphenylmethane (244 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 2 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of fluorotriphenylmethane was 15%.

Example 2

[0148] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), acetonitrile (8 mL), potassium fluoride (116 mg), and triphenylmethane (244 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 2 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of fluorotriphenylmethane was 80%.

Example 3

[0149] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), nitromethane (8 mL), cesium fluoride (608 mg), and ethyl (phenylthio)acetate (196 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 2 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of ethyl α-fluoro(phenylthio)acetate was 45% and that the yield of ethyl α,α-difluoro(phenylthio)acetate was 2%.

Example 4

[0150] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), nitromethane (8 mL), cesium fluoride (608 mg), and ethyl (phenylthio)acetate (196 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 4 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of ethyl α-fluoro(phenylthio)acetate was 7% and the yield of ethyl α,α-difluoro(phenylthio)acetate was 23%.

Example 5

[0151] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), acetonitrile (8 mL), cesium fluoride (304 mg), and bis(phenylthio)diphenylmethane (385 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 4 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of difluorodiphenylmethane was 28%.

Example 6

[0152] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), acetonitrile (8 mL), cesium fluoride (304 mg), and 2,2-diphenyl-1,3-dithiolane (258 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 4 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of difluorodiphenylmethane was 20%.

Example 7

[0153] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), acetonitrile (8 mL), cesium fluoride (304 mg), and ethyl (4-methoxyphenyl)acetate (194 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 4 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of ethyl α-fluoro(4-methoxyphenyl)acetate was 5% and that the yield of ethyl α,α-difluoro(4-methoxyphenyl)acetate was 20%.

Example 8

[0154] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), acetonitrile (8 mL), cesium fluoride (304 mg), and 2-phenoxy-2-(phenylthio)acetonitrile (60 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 4 F/mol. After completion of the electrolysis, quantification by ^{19}F NMR revealed that the yield of 2-fluoro-2-phenoxy-2-(phenylthio)acetonitrile was 40%.

Example 9

[0155] 1,1,1,3,3,3-Hexafluoro-2-propanol, acetonitrile, cesium fluoride, and 4-bromocumene were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed under an air atmosphere, thereby obtaining 1-bromo-4-(1-fluoro-1-methylethyl)benzene.

Example 10

[0156] 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mL), acetonitrile (8 mL), cesium fluoride (304 mg), and diglyme (70 mg) were placed in a diaphragm-free cell with platinum plates connected thereto as electrodes, and constant-current electrolysis was performed at 5 mA/cm^2 under an air atmosphere at room temperature so that the total energization amount was 4 F/mol. After completion of the electrolysis, a peak of fluorinated diglyme was detected by mass spectrometry.

Claims

1. A method for producing a fluorine-containing organic compound (1), comprising step A of subjecting an organic compound (2) to electrolytic fluorination in the presence of 0.2 M or more of a metal fluoride, and a fluoroalcohol.

2. The production method according to claim 1, wherein the fluorine-containing organic compound (1) is a fluorine-containing organic compound represented by formula (1):

   $$R^1\text{-}(F)_n$$

   wherein R^1 represents an organic group, and n represents an integer of 1 or more; and
   the organic compound (2) is an organic compound represented by formula (2):
   $R^1\text{-}(H)_n$, $R^1\text{-}(SR^{1a})_n$, or $R^1\text{-}(=S)_{n/2}$
   wherein R^1 and n are as defined above, and R^{1a} represents an organic group, provided that n/2 is an integer of 1 or more.

3. The production method according to claim 2, wherein the organic group is a (hetero)hydrocarbyl group optionally having one or more substituents.

4. The production method according to claim 2 or 3, wherein n is an integer of 2 or more.

5. The production method according to any one of claims 2 to 4, wherein R^1 is a polyether group.

6. The production method according to claim 1, wherein the fluorine-containing organic compound (1) is a ketone, an imine, a sulfide, an aromatic compound, a thiocarbonyl compound, or a polyether.

7. The production method according to any one of claims 1 to 6, wherein the metal fluoride is at least one metal fluoride selected from the group consisting of fluorides of metals belonging to Group 1 of the periodic table and fluorides of metals belonging to Group 2 of the periodic table.

8. The production method according to claim 7, wherein the metal fluoride is at least one metal fluoride selected from the group consisting of lithium fluoride, sodium fluoride, potassium fluoride, and cesium fluoride.

9. The production method according to any one of claims 1 to 8, wherein the fluoroalcohol is a C_{1-14} fluoroalcohol.

10. The production method according to claim 9, wherein the fluoroalcohol is a fluoroalcohol having a fluorine content within the range of 50 to 80 mass%.

11. The production method according to any one of claims 1 to 10, wherein step A is performed in the presence of an organic solvent, and the total volume of the fluoroalcohol and the organic solvent per mole of the organic compound (2) at the start of the electrolytic fluorination in step A is within the range of 0.1 to 100 L.

12. The production method according to any one of claims 1 to 11, wherein step A is performed in the presence of an organic solvent, and the volume ratio of the fluoroalcohol to the organic solvent at the start of the electrolytic fluorination in step A is 1/100 (v/v) or more.

13. The production method according to any one of claims 1 to 12, wherein the concentration of the metal fluoride in step A is within the range of 0.2 to 5 M.

14. The production method according to any one of claims 1 to 13, wherein the temperature of step A is 0°C or more.

15. A composition comprising 0.2 M or more of a metal fluoride, a fluoroalcohol, and an organic solvent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2021/000542

A. CLASSIFICATION OF SUBJECT MATTER
C25B 3/28(2021.01)i
FI: C25B3/08

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)
C25B3/28

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2021
Registered utility model specifications of Japan	1996-2021
Published registered utility model applications of Japan	1994-2021

Electronic data base consulted during the international search (name of data base and, where practicable, 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.
X Y	HFIPを溶媒として用いるスルフィド類の電解フッ素化， 2014年電気化学秋季大会講演要旨集， 27 September 2014, page 170 page 170, non-official translation (“Electrochemical fluorination of sulfides using HFIP as a solvent”, Lecture abstracts of ECSJ Fall Meeting, 2014)	1-15 2-6
X Y A	HFIP中でのKFを用いるスルフィド類の電解フッ素化， 日本化学会第94春季年会(2014)講演予稿集， 12 March 2014, page 1253 page 1253, upper left column, non-official translation (“Electrochemical fluorination of sulfides with KF in HFIP”, Lecture preprints of the 94st Spring Annual Meeting of CSJ 2014)	1-10, 13-14 2-6 11-12, 15

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*	Special categories of cited documents:
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"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
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Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2021/000542

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	無機フッ化物塩を用いる選択的な電解フッ素化，電気化学会第78回大会講演要旨集，29 March 2011, page 425 page 425, ("Highly Selective Electrochemical Fluorination of Organic Compounds Using Alkali-Metal Fluorides", Lecture abstracts of the 78th ECSJ Spring Meeting)	2-6 1, 7-15
Y A	支持電解質の使用量削減を志向したバイポーラ電解フッ素化法の開発，第41回フッ素化学討論会要旨集，25 October 2018, pp. 17-18 pp. 17-18, non-official translation ("Developing fluorination method of bipolar electrolysis aimed at reducing consumption of supporting electrolytes", Abstracts of the 41st Fluorine Conference of Japan)	2-6 1, 7-15
A	JP 2006-348381 A (ASAHI KASEI CORPORATION) 28 December 2006 (2006-12-28)	1-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2021/000542

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
JP 2006-348381 A	28 Dec. 2006	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

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