

DESCRIPTION

Title of Invention: METHOD FOR PRODUCING PERFLUOROALKYNE COMPOUND

Technical Field

5 [0001]

The present disclosure relates to a method for producing a perfluoroalkyne compound.

Background Art

10 [0002]

Perfluoroalkyne compounds are useful compounds as cleaning gases, building blocks for organic synthesis, etc., in addition to being useful as dry etching gases for semiconductors; and have a triple bond between carbon atoms. In particular, 1,1,1,4,4,4-hexafluoro-2-butyne, which has four carbon atoms, is used in various applications.

[0003]

As a method for producing a perfluoroalkyne compound, there is a method in which, using N,N-dimethylformamide, N,N-diethylformamide, 1,3-dimethyl-2-imidazolidinone, and the like as solvents, a dechlorination reaction is performed in the presence of zinc, thus obtaining 1,1,1,4,4,4-hexafluoro-2-butene from 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (1316mxx) (see, for example, Patent Literature 1).

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Citation List

Patent Literature

[0004]

PTL 1: Specification of Chinese Patent Application No. 106008147

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Summary of Invention

Technical Problem

[0005]

35 An object of the present disclosure is to provide a

method for obtaining a perfluorocarbon compound having a double bond or a triple bond at high yield.

Solution to Problem

5 [0006]

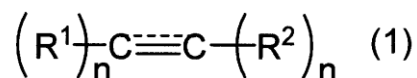
The present disclosure includes the following structure.

[0007]

Item 1.

10 A method for producing a perfluorocarbon compound represented by formula (1):

[0008]



wherein

15 a bond indicated by a double line and a dotted line is a double bond or a triple bond,

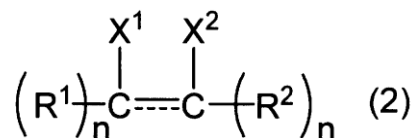
if the bond indicated by the double line and the dotted line is a double bond, both ns represent 2, and if the bond indicated by the double line and the dotted line is a triple

20 bond, both ns represent 1, and

R^1 and R^2 are the same or different, and each represents a fluorine atom or a perfluoroalkyl group,

the method comprising the step of reacting a halogenated hydrocarbon compound represented by formula (2),

25 [0009]



wherein

a bond indicated by a solid line and a dotted line is a single bond or a double bond,

30 if the bond indicated by the solid line and the dotted line is a single bond, both ns represent 2, and if the bond indicated by the solid line and the dotted line is a double bond,

both ns represent 1,

R^1 and R^2 are as defined above, and

X^1 and X^2 are the same or different, and each represents a halogen atom,

5 in an organic solvent in the presence of an iodine-containing inorganic material and zinc or a zinc alloy, to obtain a perfluorocarbon compound represented by formula (1).

[0010]

Item 2.

10 The production method according to Item 1, wherein the amount of the iodine-containing inorganic material is 0.0005 mol or more per mol of the zinc or a zinc alloy.

[0011]

Item 3.

15 The production method according to Item 1 or 2, wherein the iodine-containing inorganic material is at least one member selected from the group consisting of iodine, metal iodides, and iodine-containing interhalogen compounds.

[0012]

20 Item 4.

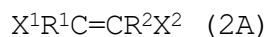
A method for producing a perfluoroalkyne compound represented by formula (1A):



wherein

25 R^1 and R^2 are the same or different, and each represents a fluorine atom or a perfluoroalkyl group,

the method comprising the step of reacting a halogenated alkene compound represented by formula (2A):



30 wherein

R^1 and R^2 are as defined above, and

X^1 and X^2 are the same or different, and each represents a halogen atom,

in at least one nitrogen-containing polar organic solvent

35 selected from the group consisting of N,N-dimethylacetamide, N,N-

diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-
3,4,5,6-tetrahydropyrimidinone, triamide hexamethylphosphate,
amine compounds, pyridine compounds, and quinoline compounds in
the presence of zinc or a zinc alloy, to obtain a perfluoroalkyne
5 compound represented by formula (1A).

[0013]

Item 5.

The production method according to any one of Items 1
to 4, wherein the reaction temperature is 0 to 250°C.

10 [0014]

Item 6.

A composition comprising:

a perfluoroalkyne compound represented by formula (1A):



15 wherein

R^1 and R^2 are the same or different, and each
represents a fluorine atom or a perfluoroalkyl group, and
a compound represented by formula (3):



20 wherein

R^1 and R^2 are as defined above.

[0015]

Item 7.

The composition according to Item 6, wherein the amount
25 of the perfluoroalkyne compound represented by formula (1A) is 85
to 99.9 mol% based on the total amount of the composition defined
as 100 mol%.

[0016]

Item 8.

30 The composition according to Item 6 or 7, which is used
as a cleaning gas, an etching gas, or a building block for
organic synthesis.

Advantageous Effects of Invention

35 [0017]

According to the present disclosure, a perfluorocarbon compound having a double bond or a triple bond can be obtained at high yield.

5 Description of Embodiments

[0018]

In the present specification, the term "comprise" is a concept including "comprising," "consisting essentially of," and "consisting of." In the present specification, the numerical
10 range indicated by "A to B" means A or more and B or less.

[0019]

In the present disclosure, "selectivity" means the ratio (mol%) of the total molar amount of the target compound contained in the effluent gas from the reactor outlet, based on
15 the total molar amount of compounds other than the raw material compound in the effluent gas.

[0020]

In the present disclosure, "conversion rate" means the ratio (mol%) of the total molar amount of compounds other than
20 the raw material compound contained in the effluent gas from the reactor outlet, based on the molar amount of the raw material compound supplied to the reactor.

[0021]

Conventionally, according to the method of Patent
25 Literature 1, 1,1,1,4,4,4-hexafluoro-2-butene has been obtained from 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (1316mxx) by performing a dechlorination reaction using N,N-dimethylformamide, N,N-diethylformamide, 1,3-dimethyl-2-imidazolidinone, and the like as solvents in the presence of zinc; however, the yield
30 thereof was only 62% at maximum.

[0022]

Thus, the conventional method does not attain sufficient yield. According to the production method of the present disclosure, a perfluoroalkyne compound can be synthesized
35 at high yield as compared to conventional methods. It is also

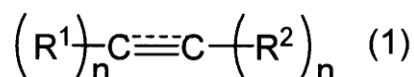
possible to synthesize a perfluoroalkene compound at high yield by the same method.

[0023]

1. Production Method of Perfluorocarbon Compound

5 The method for producing a perfluoroalkyne compound in the first embodiment of the present disclosure is a method for producing a perfluorocarbon compound represented by formula (1):

[0024]

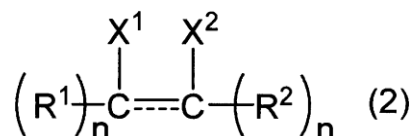


10 wherein

 a bond indicated by a double line and a dotted line is a double bond or a triple bond, if the bond indicated by the double line and the dotted line is a double bond, both ns represent 2, and if the bond indicated by the double line and the dotted line is a triple bond, both ns represent 1, and R¹ and R² are the same or different, and each represents a fluorine atom or a perfluoroalkyl group.

 The method comprises the step of reacting a halogenated hydrocarbon compound represented by formula (2):

20 [0025]



 wherein a bond indicated by a solid line and a dotted line is a single bond or a double bond, if the bond indicated by the solid line and the dotted line is a single bond, both ns represent 2, and if the bond indicated by the solid line and the dotted line is a double bond, both ns represent 1, R¹ and R² are as defined above, and X¹ and X² are the same or different, and each represents a halogen atom, in an organic solvent in the presence of an iodine-containing inorganic material and zinc or a zinc alloy, to obtain a perfluorocarbon compound represented by formula (1).

[0026]

Specifically, the method for producing the present disclosure includes the following two methods: a method for obtaining a perfluoroalkyne compound represented by formula (1A): $R^1C\equiv CR^2$ (1A), wherein R^1 and R^2 are as defined above, using as a substrate a perfluoroalkene compound represented by formula (2A): $X^1R^1C=CR^2X^2$ (2A), wherein R^1 , R^2 , X^1 , and X^2 are as defined above; and a method for obtaining a perfluoroalkene compound represented by formula (1B): $(R^1)_2C=C(R^2)_2$ (1B), wherein R^1 and R^2 are as defined above, using as a substrate a perfluoroalkane compound represented by formula (2B): $(R^1)_2X^1C-C(R^2)_2X^2$ (2B), wherein R^1 , R^2 , X^1 , and X^2 are as defined above.

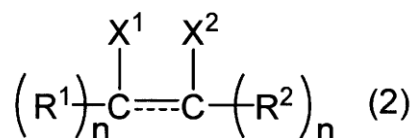
[0027]

According to the present disclosure, by performing a dehalogenation reaction of the halogenated hydrocarbon compound represented by formula (2) in the presence of an iodine-containing inorganic material and zinc or a zinc alloy in an organic solvent, X^1 and X^2 are desorbed from the halogenated hydrocarbon compound represented by formula (2), thus obtaining a perfluorocarbon compound represented by formula (1) above.

[0028]

As described above, the halogenated hydrocarbon compound that can be used in the production method of the present disclosure as a substrate is a halogenated hydrocarbon compound represented by formula (2):

[0029]



wherein a bond indicated by a solid line and a dotted line is a single bond or a double bond, if the bond indicated by the solid line and the dotted line is a single bond, both n s represent 2, and if the bond indicated by the solid line and the dotted line is a double bond, both n s represent 1, R^1 and R^2 are the same or different, and each represents a fluorine atom or a perfluoroalkyl group, and X^1 and X^2 are the same or different, and

each represents a halogen atom.

[0030]

In formula (2), the perfluoroalkyl group indicated by R^1 and R^2 means an alkyl group in which all of the hydrogen atoms are replaced with a fluorine atom. The perfluoroalkyl group is, for example, a perfluoroalkyl group having 1 to 20 carbon atoms, preferably 1 to 12 carbon atoms, more preferably 1 to 6 carbon atoms, even more preferably 1 to 4 carbon atoms, and particularly preferably 1 to 3 carbon atoms. The perfluoroalkyl group is preferably a linear or branched perfluoroalkyl group. Preferable examples of the perfluoroalkyl group include a trifluoromethyl group (CF_3-), a pentafluoroethyl group (C_2F_5-), and the like.

[0031]

In formula (2), examples of the halogen atom represented by X^1 and X^2 include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. However, from the viewpoint of easily obtaining the perfluorocarbon compound represented by formula (1) by the production method of the present disclosure, the use of a substrate that is free of iodine is preferred. From such a viewpoint, a fluorine atom, a chlorine atom, and a bromine atom are preferred as a halogen atom represented by X^1 and X^2 . However, from the viewpoint of easily obtaining the perfluorocarbon compound represented by formula (1) above by the production method of the present disclosure, it is particularly preferable that both X^1 and X^2 not be fluorine atoms simultaneously. Specifically, it is preferable that at least one of X^1 and X^2 be a chlorine atom or a bromine atom.

[0032]

In the halogenated hydrocarbon compound, which is a substrate, it is particularly preferable that both R^1 and R^2 be trifluoromethyl groups, and that both X^1 and X^2 be chlorine atoms, from the viewpoint of production at high conversion, high yield, and high selectivity.

[0033]

R^1 and R^2 described above may be the same or different.

R¹s may be the same or different from each other. R²s may be the same or different from each other. X¹ and X² described above may be the same or different.

[0034]

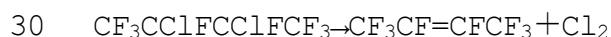
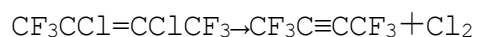
5 Examples of the halogenated hydrocarbon compound that is used as a substrate satisfying the above conditions include halogenated alkene compounds, such as CFCl=CFCl, CFBr=CFBr, CFCl=CFBr, CF₃CCl=CClCF₃, CF₃CCl=CBrCF₃, CF₃CBr=CBrCF₃, C₂F₅CCl=CClC₂F₅, C₂F₅CCl=CBrC₂F₅, and C₂F₅CBr=CBrC₂F₅; and
10 halogenated alkane compounds, such as CF₂ClCF₂Cl, ClCF₂CF₂Br, CF₂BrCF₂Br, CF₃CClFCClFCF₃, CF₃CBrFCBrFCF₃, (CF₃)₂CClCCl(CF₃)₂, (CF₃)₂CClCBr(CF₃)₂, (CF₃)₂CBrCBr(CF₃)₂, (C₂F₅)₂CClCCl(C₂F₅)₂, (C₂F₅)₂CClCBr(C₂F₅)₂, and (C₂F₅)₂CBrCBr(C₂F₅)₂. These halogenated hydrocarbon compounds can be used alone, or in a combination of
15 two or more. As the halogenated hydrocarbon compound, a known product or a commercially available product can be used.

[0035]

 In the step of obtaining a perfluorocarbon compound from a halogenated hydrocarbon compound according to the present
20 disclosure, for example, in the halogenated hydrocarbon compound represented by formula (2) used as a substrate, both R¹ and R² are particularly preferably a fluorine atom or a trifluoromethyl group; and both X¹ and X² are particularly preferably a chlorine atom.

25 [0036]

 Specifically, a dehalogenation reaction (particularly a dechlorination reaction) according to the following reaction formulae:



is preferred.

[0037]

 The production method in the first embodiment of the present disclosure includes the step of reacting the halogenated
35 hydrocarbon compound represented by formula (2) in an organic

solvent in the presence of an iodine-containing inorganic material and zinc or a zinc alloy, to obtain a perfluorocarbon compound represented by formula (1).

[0038]

5 In this case, from the viewpoint of the yield and selectivity of the perfluorocarbon compound, the amount of the halogenated hydrocarbon compound represented by formula (2) is preferably 0.05 to 30 mol, more preferably 0.1 to 10 mol, even more preferably 0.2 to 5 mol per mol of zinc or a zinc alloy
10 described below.

[0039]

 In the present invention, by using the iodine-containing inorganic material, the surface of the zinc or a zinc alloy is activated to promote the reaction of the halogenated
15 hydrocarbon compound represented by formula (2), thereby obtaining the halogenated hydrocarbon compound represented by formula (2) at high yield.

 The iodine-containing inorganic material to be used can be any inorganic material that contains an iodine atom. Examples
20 of iodine-containing inorganic materials include iodine and metal iodides such as representative metal iodides (e.g., sodium iodide, potassium iodide, magnesium iodide, and calcium iodide), and transition metal iodides (e.g., zinc iodide); iodine-containing interhalogen compounds (e.g., iodine fluoride, iodine
25 chloride, iodine bromide), and the like. The production method according to the present disclosure may produce zinc halide (a mixture of zinc fluoride, zinc chloride, and zinc iodide) as impurities in the product. The zinc halide contained in the product as impurities can be used as an iodine-containing
30 inorganic material, and can be recycled in the production method according to the present disclosure. These iodine-containing inorganic materials can be used singly, or in a combination of two or more. In particular, from the viewpoint of the yield and the selectivity of the perfluorocarbon compound represented by
35 formula (1), the iodine-containing inorganic material is

preferably iodine, a representative metal iodide, a transition metal iodide, an iodine-containing interhalogen compound; preferably iodine, a representative metal iodide, an iodine-containing interhalogen compound; and even more preferably iodine. The use of an iodine-free material, such as zinc fluoride or zinc chloride, as a halogen-containing material instead of an iodine-containing inorganic material does not provide the effect of increasing the yield and selectivity of the perfluorocarbon compound represented by formula (1).

10 [0040]

The amount of the iodine-containing inorganic material is preferably 0.0005 mol or more, and more preferably 0.001 mol or more per mol of the zinc or a zinc alloy described below from the viewpoint of the yield and selectivity of the perfluorocarbon compound represented by formula (1).

15

Although there is no limitation on the upper limit of the amount of the iodine-containing inorganic material, it is typically preferably 2 mol or less, and more preferably 0.1 mol or less per mol of the zinc or a zinc alloy described below from the viewpoint of the yield, selectivity, and cost of the perfluorocarbon compound represented by formula (1).

20

[0041]

The amount of the iodine-containing inorganic material is preferably 0.00002 mol or more, and more preferably 0.00005 mol or more per mol of the organic solvent described below from the viewpoint of the yield, selectivity, and cost of the perfluorocarbon compound represented by formula (1). Although there is no limitation on the upper limit of the amount of the iodine-containing inorganic material, it is typically preferably equal to or lower than the solubility of the organic solvent described below, and more preferably 0.08 mol or less per mol of the organic solvent described below from the viewpoint of the yield, selectivity, and cost of the perfluorocarbon compound represented by formula (1).

30

35 [0042]

Examples of elements usable in the zinc alloy of the "zinc or a zinc alloy" include lead, cadmium, and iron. Commercially available zinc may contain impurities such as lead, cadmium, and iron. The present disclosure includes a zinc alloy
5 that contains these impurities.

[0043]

The organic solvent is preferably a polar organic solvent, particularly from the viewpoint of dissolving the halogenated hydrocarbon compound represented by formula (2). From
10 the viewpoint of the yield and selectivity of the perfluorocarbon compound represented by formula (1), a nitrogen-containing polar solvent is preferred. Examples of such organic solvents include amide compounds (N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N,N-diisopropylformamide, N-methyl-2-
15 pyrrolidone, 1,3-dimethyl-2-imidazolidinone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, and hexamethylphosphoric triamide), amine compounds (triethylamine and 1-methylpyrrolidine), pyridine compounds (pyridine and methylpyridine), quinoline compounds (quinoline and
20 methylquinoline), and the like. These organic solvents can be used alone, or in a combination of two or more. Of these, amide compounds are preferred from the viewpoint of obtaining a perfluoroalkyne compound at high yield; N,N-dimethylformamide, N,N-diethylformamide, N,N-diisopropylformamide, N-methyl-2-
25 pyrrolidone, 1,3-dimethyl-2-imidazolidinone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, and hexamethylphosphoric triamide are more preferred; N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, and hexamethylphosphoric triamide are even more preferred; and N-
30 methyl-2-pyrrolidone is particularly preferred.

[0044]

The amount of the organic solvent can be any amount that is a solvent amount, and is preferably 0.01 to 20 mol, and more preferably 0.1 to 10 mol per mol of zinc or a zinc alloy
35 from the viewpoint of the yield and selectivity of the

perfluorocarbon compound represented by formula (1).

[0045]

In the present disclosure, from the viewpoint of the yield and selectivity of the perfluorocarbon compound represented by formula (1), it is particularly preferable to use N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, and hexamethylphosphoric triamide (particularly N-methyl-2-pyrrolidone) as the organic solvent, and use an iodine-containing inorganic material.

[0046]

According to the production method of the present disclosure, the halogenated hydrocarbon compound represented by formula (2) is reacted in an organic solvent, in the presence of an iodine-containing inorganic material and zinc or a zinc alloy. The order for adding each component is not limited. The components can be added simultaneously or sequentially.

[0047]

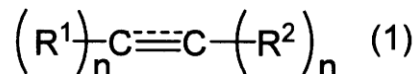
The reaction atmosphere is not limited. From the viewpoint of the yield and selectivity of the perfluorocarbon compound represented by formula (1), an inert gas atmosphere (nitrogen gas atmosphere, argon gas atmosphere, etc.) is preferred. The reaction temperature is not limited. From the viewpoint of the yield and selectivity of the perfluorocarbon compound represented by formula (1), it is preferably 0 to 250°C, and more preferably 20 to 200°C. The reaction time (retention time at a highest temperature reached) can be a time period such that the reaction sufficiently proceeds. From the viewpoint of the yield and selectivity of the perfluorocarbon compound represented by formula (1), it is preferably 0.5 to 20 hours, and more preferably 1 to 10 hours. After the completion of the reaction, purification treatment is performed according to an ordinary method to obtain a perfluorocarbon compound represented by formula (1).

[0048]

The target compound of the present disclosure thus

obtained is a perfluorocarbon compound represented by formula (1):

[0049]



5 wherein the bond indicated by a double line and a dotted line is a double bond or a triple bond; if the bond indicated by the double line and the dotted line is a double bond, both ns represent 2, and if the bond indicated by the double line and the dotted line is a triple bond, both ns represent 1; and R¹ and R²
10 are the same or different, and each represents a fluorine atom or a perfluoroalkyl group.

[0050]

R¹ and R² in formula (1) correspond to R¹ and R² in formula (2) described above. Accordingly, specific examples of
15 the perfluorocarbon compound represented by formula (1) to be produced include perfluoroalkyne compounds such as CF≡CF, CF₃C≡CCF₃, and C₂F₅C≡CC₂F₅; and perfluoroalkene compounds, such as CF₂=CF₂, C(CF₃)₂=C(CF₃)₂, and C(C₂F₅)₂=C(C₂F₅)₂.

[0051]

20 According to the production method of the present disclosure, the yield and selectivity of the perfluorocarbon compound represented by formula (1) can be increased.

[0052]

The perfluorocarbon compound of formula (1) obtained as
25 described above can be effectively used in various applications, including an etching gas for forming state-of-the-art microstructures, such as semiconductors and liquid crystals; cleaning gas; and building blocks for organic synthesis. The details of the building blocks for organic synthesis are
30 described later.

[0053]

2. Production Method of Perfluoroalkyne Compound

The production method of a perfluoroalkyne compound in the second embodiment of the present disclosure is a method for

producing a perfluoroalkyne compound represented by formula (1A):
 $R^1C\equiv CR^2$ (1A)

wherein R^1 and R^2 are the same or different, and each represents a fluorine atom or a perfluoroalkyl group.

5 The method comprises the step of reacting a halogenated alkene compound represented by formula (2A): $X^1R^1C=CR^2X^2$ (2A), wherein R^1 and R^2 are as defined above, X^1 and X^2 are the same or different, and each represents a halogen atom, in at least one nitrogen-containing polar organic solvent selected from the group
10 consisting of N,N-dimethylacetamide, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, triamide hexamethylphosphate, amine compounds, pyridine compounds, and quinoline compounds in the presence of zinc or a zinc alloy, to obtain a perfluoroalkyne
15 compound represented by formula (1A).

[0054]

According to the present disclosure, by performing a dehalogenation reaction of the halogenated alkene compound represented by formula (2A) in at least one nitrogen-containing
20 polar organic solvent selected from the group consisting of N,N-dimethylacetamide, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, triamide hexamethylphosphate, amine compounds, pyridine compounds, and quinoline compounds in the presence of zinc or a
25 zinc alloy, X^1 and X^2 are desorbed from the halogenated alkene compound represented by formula (2A) to obtain a perfluoroalkyne compound represented by formula (1A) above.

[0055]

The halogenated alkene compound that can be used as a
30 substrate in the production method of the present disclosure can be the same as those described above in section "1. Production Method of Perfluorocarbon Compound." The specific preferable examples can also be the same.

[0056]

35 The production method in the second embodiment of the

present disclosure includes the step of reacting the halogenated alkene compound represented by formula (2A) in at least one nitrogen-containing polar organic solvent selected from the group consisting of N,N-dimethylacetamide, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, triamide hexamethylphosphate, amine compounds, pyridine compounds, and quinoline compounds, in the presence of zinc or a zinc alloy, to obtain a perfluoroalkyne compound represented by formula (1A).

10 [0057]

In this case, the amount of the halogenated alkene compound represented by formula (2A), which is a substrate, can be the same as that described above in section "1. Production Method of Perfluorocarbon Compound" as the amount of the halogenated hydrocarbon compound represented by formula (2). The specific preferable examples can also be the same.

[0058]

The zinc or zinc alloy can be the same as those described above in section "1. Production Method of Perfluorocarbon Compound." The specific preferable examples can also be the same.

[0059]

The reaction of the halogenated alkene compound represented by formula (2A) can also be performed in the presence of an iodine-containing inorganic material. This can further improve the yield and selectivity of the perfluoroalkyne compound represented by formula (1A). The iodine-containing material can be the same as those described above in section "1. Production Method of Perfluorocarbon Compound." The specific preferable examples and amounts can also be the same.

[0060]

As at least one nitrogen-containing polar organic solvent selected from the group consisting of N,N-dimethylacetamide, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone,

35

triamide hexamethylphosphate, amine compounds, pyridine compounds, and quinoline compounds, nitrogen-containing polar organic solvents can be used alone, or in a combination of two or more. Of these, from the viewpoint of the yield and selectivity of the perfluoroalkyne compound, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, and hexamethylphosphoric acid triamide are preferred, and N-methyl-2-pyrrolidone is more preferred.

[0061]

The amount of at least one nitrogen-containing polar organic solvent selected from the group consisting of N,N-dimethylacetamide, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, hexamethylphosphoric acid triamide, amine compounds, pyridine compounds, and quinoline compounds can be any amount that is a solvent amount. From the viewpoint of obtaining the perfluoroalkyne compound at higher yield, the amount of at least one nitrogen-containing polar organic solvent is preferably 0.01 to 20 mol, and more preferably 0.1 to 10 mol, per mol of zinc or a zinc alloy.

[0062]

In the present disclosure, from the viewpoint of the yield and selectivity of the perfluoroalkyne compound, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, and hexamethylphosphoric acid triamide (particularly N-methyl-2-pyrrolidone) are used as organic solvents; and it is particularly preferable to use an iodine-containing inorganic material.

[0063]

In the production method of the present disclosure, the halogenated alkene compound represented by formula (2A) is reacted in an organic solvent in the presence of zinc or a zinc alloy, and optionally an iodine-containing inorganic material. The order for adding each component is not limited. The components can be added simultaneously or sequentially.

[0064]

The reaction atmosphere is not limited. From the viewpoint of obtaining the perfluoroalkyne compound at higher yield, an inert gas atmosphere (e.g., nitrogen gas atmosphere or argon gas atmosphere) is preferred. The reaction temperature is not limited; and from the viewpoint of the yield and selectivity of the perfluoroalkyne compound, it is preferably 0 to 250°C, and more preferably 20 to 200°C. The reaction time (retention time at a highest temperature reached) can be a time period such that the reaction sufficiently proceeds; and from the viewpoint of the yield and selectivity of the perfluoroalkyne compound, it is preferably 0.5 to 20 hours, and more preferably 1 to 10 hours. After the completion of the reaction, purification treatment is performed according to an ordinary method to obtain a perfluoroalkyne compound represented by formula (1A).

[0065]

The target compounds of the present disclosure obtained in this manner can be the same as those described above in section "1. Production Method of Perfluorocarbon Compound (Part 1)" as perfluoroalkyne compounds.

[0066]

According to the production method of the present disclosure, the yield and selectivity of the perfluoroalkyne compound represented by formula (1A) can be increased.

[0067]

The perfluoroalkyne compound of formula (1A) obtained as described above can be effectively used in various applications, including an etching gas for forming state-of-the-art microstructures, such as semiconductors and liquid crystals; a cleaning gas; and building blocks for organic synthesis. The details of the building blocks for organic synthesis are described later.

[0068]

3. Perfluoroalkyne Composition

The perfluoroalkyne compound can be obtained according

to the first or second embodiment described above, and may be obtained in the form of a composition containing the perfluoroalkyne compound represented by formula (1A). For example, it can be obtained in the form of a composition

5 (perfluoroalkyne composition) comprising the perfluoroalkyne compound represented by formula (1A) and the compound represented by formula (3): $R^1CH=CHR^2$ (3), wherein R^1 and R^2 are as defined above.

[0069]

10 The composition may comprise the compound represented by formula (4): $R^3C\equiv CR^4$ (4), wherein R^3 and R^4 each represents a fluoroalkyl group having one hydrogen atom, and the compound represented by formula (5): $X^1R^1C=CHR^2$ (5), wherein R^1 , R^2 , and X^1 are as defined above.

15 [0070]

In formulae (1A), (3), and (5), perfluoroalkyl groups represented by R^1 and R^2 mean alkyl groups in which all of the hydrogen atoms are substituted with a fluorine atom. Such perfluoroalkyl groups have, for example, 1 to 20 carbon atoms, preferably 1 to 12 carbon atoms, more preferably 1 to 6 carbon atoms, even more preferably 1 to 4 carbon atoms, and particularly preferably 1 to 3 carbon atoms. The perfluoroalkyl group is preferably a linear or branched perfluoroalkyl group. Preferable examples of the perfluoroalkyl group include a trifluoromethyl group (CF_3-), a pentafluoroethyl group (C_2F_5-), and the like.

25 [0071]

The fluoroalkyl group having one or more hydrogen atom represented by R^3 and R^4 in formula (4) is a fluoroalkyl group in which one fluorine atom is replaced with a hydrogen atom in the perfluoroalkyl group in which all of the hydrogen atoms are replaced with a fluorine atom. The fluoroalkyl group preferably has one hydrogen atom having, for example, 1 to 20 carbon atoms, preferably 1 to 12 carbon atoms, more preferably 1 to 6 carbon atoms, even more preferably 1 to 4 carbon atoms, and particularly preferably 1 to 3 carbon atoms. The fluoroalkyl group is

35

preferably a linear or branched fluoroalkyl group. The fluoroalkyl group is preferably a difluoromethyl group ($\text{CF}_2\text{H}-$) or a tetrafluoroethyl group ($\text{CF}_3\text{CFH}-$ and CF_2HCF_2-).

[0072]

5 In formula (5), the halogen atom represented by X^1 includes a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. However, from the viewpoint of easily obtaining the perfluoroalkyne compound represented by formula (1A) described above by the production method of the present disclosure, it is
10 preferable to use a substrate that does not contain iodine. From this viewpoint, a fluorine atom, a chlorine atom, and a bromine atom are preferred as the halogen atom represented by X^1 .

[0073]

 In this perfluoroalkyne composition of the present
15 disclosure, the amount of the perfluoroalkyne compound represented by formula (1A) is preferably 85 to 99.9 mol% (particularly 90 to 99.8 mol%), the amount of the compound represented by formula (3) is preferably 0.3 to 15 mol% (particularly from 0.5 to 8 mol%), the amount of the compound
20 represented by formula (4) is preferably 0.20 to 2.00 mol% (particularly 1.10 to 1.80 mol%), and the amount of the compound represented by formula (5) is preferably 0.2 to 3.0 mol% (particularly 0.25 to 2.5 mol%), based on the total amount of the perfluoroalkyne composition of the present disclosure defined as
25 100 mol%.

[0074]

 In the production method according to the present disclosure, the perfluoroalkyne compound represented by formula (1A) can be obtained at high yield as described above, even when
30 it is obtained as a perfluoroalkyne composition. Therefore, the components other than the perfluoroalkyne compound represented by formula (1A) in the perfluoroalkyne composition can be reduced, and the labor required for purification to obtain a perfluoroalkyne compound represented by formula (1A) can thus be
35 reduced.

[0075]

The perfluoroalkyne composition of the present disclosure can also be effectively used for various applications, such as an etching gas used for forming state-of-the-art microstructures (e.g., semiconductors and liquid crystals), a building block for organic synthesis, and a cleaning gas. The term "building block for organic synthesis" means a substance that can serve as a precursor for a compound having a highly reactive skeleton. For example, the perfluoroalkyne composition of the present disclosure can be converted into a substance that can serve as a detergent or a fluorine-containing medicinal intermediate by reacting with a fluorine-containing organosilicon compound, such as $\text{CF}_3\text{Si}(\text{CH}_3)_3$, and introducing fluoroalkyl, such as a CF_3 group.

15 [0076]

Embodiments according to the present disclosure are described above; however, various changes in forms and details can be made without departing from the spirit and scope of the claims.

20

Examples

[0077]

The features of the present disclosure are clarified below with reference to Examples. However, the present disclosure is not limited to the Examples.

25

[0078]

In the method for producing halogenated alkyne compounds of Examples 1 to 6 and Comparative Examples 1 to 3, a perfluoroalkyne compound was obtained by a dechlorination reaction according to the following reaction formula:
$$\text{CF}_3\text{CCl}=\text{CClCF}_3 \rightarrow \text{CF}_3\text{C}\equiv\text{CCF}_3 + \text{Cl}_2$$
using as a raw material compound the halogenated alkene compound represented by formula (2A), wherein R^1 and R^2 each represents a trifluoromethyl group, and X^1 and X^2 each represents a chlorine atom.

35 [0079]

In the method for producing halogenated alkene compounds of Example 7 and Comparative Example 4, a perfluoroalkene compound was obtained by a dechlorination reaction according to the following reaction formula:

- 5 $\text{CF}_3\text{CClFCClFCF}_3 \rightarrow \text{CF}_3\text{CF}=\text{CFCF}_3 + \text{Cl}_2$, using as a raw material compound the halogenated alkane compound represented by formula (2B), wherein R^1 and R^2 each represents a trifluoromethyl group, and X^1 and X^2 each represents a chlorine atom.

[0080]

10 Example 1 (Alkyne Synthesis): DMF; I_2 1 mol%

An eggplant flask equipped with a condenser, to which a trap was connected, was cooled to -78°C ; and 10 g (0.04 mol) of $\text{CF}_3\text{CCl}=\text{CClCF}_3$ (substrate), 45 g (0.62 mol) of N,N-dimethylformamide (solvent), 3.65 g (0.056 mol) of zinc, and 0.14 g (0.0006 mol; 1 mol% for zinc) of I_2 were added to the eggplant flask. The mixture was then heated with stirring until the internal temperature reached 50°C . After the internal temperature became constant, the mixture was allowed to react with stirring for 5 hours. After completion of the reaction, the gas phase and liquid phase in the collection cylinder and the reaction mixture were analyzed by gas chromatography. The conversion and selectivity were calculated, taking into consideration the individual results of analysis. The conversion was 88.73 mol%, and the selectivity of each component was as follows: $\text{CF}_3\text{C}\equiv\text{CCF}_3$ 89.70 mol% (yield: 79.6 mol%), 1336mzz ($\text{CF}_3\text{CH}=\text{CHCF}_3$) 9.27 mol%, $\text{CF}_2\text{HC}\equiv\text{CCF}_2\text{H}$ 0.26 mol%, $\text{CF}_3\text{CF}=\text{CHCF}_3$ 0.00 mol%, $\text{CF}_3\text{CCl}=\text{CHCF}_3$ 0.57 mol%, and other by-products 0.19 mol% in total.

[0081]

Example 2 (Alkyne Synthesis): NMP; I_2 1 mol%

30 The reaction proceeded in the same manner as in Example 1, except that N-methyl-2-pyrrolidone was used as the solvent instead of N,N-dimethylformamide. After completion of the reaction, the gas phase and liquid phase in the collection cylinder and the reaction mixture were analyzed by gas chromatography. The conversion and selectivity were calculated,

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taking into consideration the individual results of analysis. The conversion was 99.1 mol%, and the selectivity of each component was as follows:

CF₃C≡CCF₃ 92.11 mol% (yield: 91.3 mol%), 1336mzz(CF₃CH=CHCF₃) 3.82
5 mol%, CF₂HC≡CCF₂H 1.58 mol%, CF₃CF=CHCF₃ 0.00 mol%, CF₃CCl=CHCF₃
0.31 mol%, and other by-products 2.18 mol% in total.
[0082]

Example 3 (Alkyne Synthesis): NMP; ZnI₂ 1 mol%

The reaction proceeded in the same manner as in Example
10 1, except that N-methyl-2-pyrrolidone was used as the solvent
instead of N,N-dimethylformamide, and ZnI₂ was used as the iodine-
containing inorganic material instead of I₂. After completion of
the reaction, the gas phase and liquid phase in the collection
cylinder and the reaction mixture were analyzed by gas
15 chromatography. The conversion and selectivity were calculated,
taking into consideration the individual results of analysis. The
conversion was 99.2 mol%, and the selectivity of each component
was as follows:

CF₃C≡CCF₃ 91.10 mol% (yield: 90.4 mol%), 1336mzz(CF₃CH=CHCF₃) 0.92
20 mol%, CF₂HC≡CCF₂H 1.33 mol%, CF₃CF=CHCF₃ 1.10 mol%, CF₃CCl=CHCF₃
1.31 mol%, and other by-products 4.24 mol% in total.
[0083]

Example 4 (Alkyne Synthesis): NMP; NaI 1 mol%

The reaction proceeded in the same manner as in Example
25 1, except that N-methyl-2-pyrrolidone was used as the solvent
instead of N,N-dimethylformamide, and NaI was used as the iodine-
containing inorganic material instead of I₂. After completion of
the reaction, the gas phase and liquid phase in the collection
cylinder and the reaction mixture were analyzed by gas
30 chromatography. The conversion and selectivity were calculated,
taking into consideration the individual results of analysis. The
conversion was 98.4 mol%, and the selectivity of each component
was as follows:

CF₃C≡CCF₃ 92.51 mol% (yield: 91.0 mol%), 1336mzz(CF₃CH=CHCF₃) 1.12
35 mol%, CF₂HC≡CCF₂H 1.19 mol%, CF₃CF=CHCF₃ 0.41 mol%, CF₃CCl=CHCF₃

0.31 mol%, and other by-products 4.46 mol% in total.

[0084]

Example 5 (Alkyne Synthesis): NMP; No Iodine-containing Inorganic Material

5 The reaction proceeded in the same manner as in Example 1, except that N-methyl-2-pyrrolidone was used as the solvent instead of N,N-dimethylformamide, and I₂ was not used. After completion of the reaction, the gas phase and liquid phase in the collection cylinder and the reaction mixture were analyzed by gas
10 chromatography. The conversion and selectivity were calculated, taking into consideration the individual results of analysis. The conversion was 99.6 mol%, and the selectivity of each component was as follows:

CF₃C≡CCF₃ 48.9 mol% (yield: 48.7 mol%), 1336mzz (CF₃CH=CHCF₃) 2.2
15 mol%, CF₂HC≡CCF₂H 2.2 mol%, CF₃CF=CHCF₃ 1.1 mol%, CF₃CCl=CHCF₃ 2.1 mol%, and other by-products 43.4 mol% in total.

[0085]

Example 6 (Alkyne Synthesis): NMP; ICL 1 mol%

 The reaction proceeded in the same manner as in Example
20 1, except that N-methyl-2-pyrrolidone was used as the solvent instead of N,N-dimethylformamide, and iodine monochloride (ICL) was used as the iodine-containing inorganic material instead of I₂. After completion of the reaction, the gas phase and liquid phase in the collection cylinder and the reaction mixture were
25 analyzed by gas chromatography. The conversion and selectivity were calculated, taking into consideration the individual results of analysis. The conversion was 99.5 mol%, and the selectivity of each component was as follows:

CF₃C≡CCF₃ 93.11 mol% (yield: 92.6 mol%), 1336mzz (CF₃CH=CHCF₃) 3.20
30 mol%, CF₂HC≡CCF₂H 0.22 mol%, CF₃CF=CHCF₃ 0.22 mol%, CF₃CCl=CHCF₃ 0.11 mol%, and other by-products 2.51 mol% in total.

[0086]

Comparative Example 1 (Alkyne Synthesis): DMF; No Iodine-containing Inorganic Material

35 The reaction proceeded in the same manner as in Example

1, except that I₂ was not used. After completion of the reaction, the gas phase and liquid phase in the collection cylinder and the reaction mixture were analyzed by gas chromatography. The conversion and selectivity were calculated, taking into
5 consideration the individual results of analysis. The conversion was 98.06 mol%, and the selectivity of each component was as follows:

CF₃C≡CCF₃ 56.20 mol% (yield: 55.1 mol%), 1336mzz (CF₃CH=CHCF₃) 0.24 mol%, CF₂HC≡CCF₂H 1.03 mol%, CF₃CF=CHCF₃ 0.35 mol%, CF₃CCl=CHCF₃
10 0.47 mol%, and other by-products 41.70 mol% in total.

[0087]

Comparative Example 2 (Alkyne Synthesis): Xylene; I₂ 1 mol%

The procedure of Example 1 was repeated, except that xylene was used as the solvent instead of N,N-dimethylformamide.
15 However, the reaction did not proceed at all, and CF₃C≡CCF₃ was not obtained.

[0088]

Comparative Example 3 (Alkyne Synthesis): Dibutyl Ether; I₂ 1 mol%

The procedure of Example 1 was repeated, except that
20 dibutyl ether was used as the solvent instead of N,N-dimethylformamide. However, the reaction did not proceed at all, and CF₃C≡CCF₃ was not obtained.

[0089]

Example 7 (Alkene Synthesis): NMP; I₂ 1 mol%

25 An eggplant flask equipped with a condenser, to which a trap was connected, was cooled to -78°C; and 10 g (0.037 mol) of CF₃CCLF-CCLFCF₃ (substrate), 45 g (0.45 mol) of N-methyl-2-pyrrolidone (solvent), 2.90 g (0.044 mol) of zinc, and 0.11 g (0.0004 mol; 1 mol% for zinc) of I₂ were added to the eggplant
30 flask. The mixture was then heated with stirring until the internal temperature reached 60°C. After the internal temperature became constant, the mixture was allowed to react with stirring for 5 hours. After completion of the reaction, the gas phase and liquid phase in the collection cylinder and the reaction mixture
35 were analyzed by gas chromatography. The conversion and

selectivity were calculated, taking into consideration the individual results of analysis. The conversion was 98.3 mol%, and the selectivity of each component was as follows:

CF₃CF=CFCF₃ 94.3 mol% (yield: 92.7 mol%), CF₃CFHCClFCF₃ 1.9 mol%,
5 CF₃CFHCFHCF₃ 0.65 mol%, CF₃CH=CFCF₃ 0.01 mol%, and other by-products 3.14 mol% in total.

[0090]

Comparative Example 4 (Alkene Synthesis): NMP; No Iodine-containing Inorganic Material

10 The reaction proceeded in the same manner as in Example 6, except that I₂ was not used. After completion of the reaction, the gas phase and liquid phase in the collection cylinder and the reaction mixture were analyzed by gas chromatography. The conversion and selectivity were calculated, taking into
15 consideration the individual results of analysis. The conversion was 87.3 mol%, and the selectivity of each component was as follows:

CF₃CF=CFCF₃ 52.4 mol% (yield: 45.7 mol%), CF₃CFHCClFCF₃ 5.3 mol%,
CF₃CFHCFHCF₃ 3.1 mol%, CF₃CH=CFCF₃ 0.1 mol%, and other by-products
20 39.1 mol% in total.

[0091]

The results of Examples 1 to 6 and Comparative Examples 1 to 3 are shown in Table 1, and the results of Example 7 and Comparative Example 4 are shown in Table 2.

25 [0092]

Table 1

	Solvent	Iodine-containing inorganic material (mol%)	Conversion (%)	Selectivity (%)						
				$\text{CF}_3\text{C}\equiv\text{CCF}_3$	$\text{CF}_3\text{CH}\equiv\text{CHCF}_3$ (1336mzz)	$\text{CF}_2\text{HC}\equiv\text{CCF}_2\text{H}$	$\text{CF}_3\text{CF}=\text{CHCF}_3$	$\text{CF}_3\text{CCl}=\text{CHCF}_3$	Others	Total
Ex.1	DMF	I_2 (1)	88.73	89.70	9.27	0.26	0.00	0.57	0.19	100
Ex.2	NMP	I_2 (1)	99.1	92.11	3.82	1.58	0.00	0.31	2.18	100
Ex.3	NMP	ZnI_2 (1)	99.2	91.10	0.92	1.33	1.10	1.31	4.24	100
Ex.4	NMP	NaI (1)	98.4	92.51	1.12	1.19	0.41	0.31	4.46	100
Ex.5	NMP	None	99.6	48.9	2.2	2.2	1.1	2.1	43.4	100
Ex.6	NMP	ICl (1)	99.5	93.11	3.20	0.22	0.22	0.11	2.51	100
Comp. Ex.1	DMF	None	98.06	56.20	0.24	1.03	0.35	0.47	41.70	100
Comp. Ex.2	Xylene	I_2 (1)	Not reacted	-	-	-	-	^	-	-
Comp. Ex.3	Dibutyl ether	I_2 (1)	Not reacted	-	-	-	-	^	-	-

[0093]

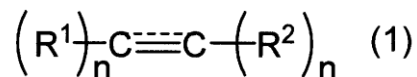
Table 2

	Solvent	Iodine- containing inorganic material (mol%)	Conversion (%)						
				$\text{CF}_3\text{CF}=\text{CFCF}_3$	$\text{CF}_3\text{CFHCCLFCF}_3$	$\text{CF}_3\text{CFHCFHCF}_3$	$\text{CF}_3\text{CH}=\text{CFCF}_3$	Others	Total
Ex. 7	NMP	I_2 (1)	98.3	94.3	1.9	0.65	0.01	3.14	100
Comp. Ex. 4	NMP	None	87.3	52.4	5.3	3.1	0.1	29.1	100

CLAIMS

[Claim 1]

A method for producing a perfluorocarbon compound
5 represented by formula (1):



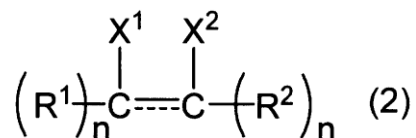
wherein

a bond indicated by a double line and a dotted line is
a double bond or a triple bond,

10 if the bond indicated by the double line and the dotted
line is a double bond, both ns represent 2, and if the bond
indicated by the double line and the dotted line is a triple
bond, both ns represent 1, and

R^1 and R^2 are the same or different, and each
15 represents a fluorine atom or a perfluoroalkyl group,

the method comprising the step of reacting a
halogenated hydrocarbon compound represented by formula (2),



wherein

20 a bond indicated by a solid line and a dotted line is a
single bond or a double bond,

if the bond indicated by the solid line and the dotted
line is a single bond, both ns represent 2, and if the bond
indicated by the solid line and the dotted line is a double bond,
25 both ns represent 1,

R^1 and R^2 are as defined above, and

X^1 and X^2 are the same or different, and each
represents a halogen atom,
in an organic solvent in the presence of an iodine-containing
30 inorganic material and zinc or a zinc alloy, to obtain a
perfluorocarbon compound represented by formula (1).

[Claim 2]

The production method according to claim 1, wherein the amount of the iodine-containing inorganic material is 0.0005 mol or more per mol of the zinc or zinc alloy.

5

[Claim 3]

The production method according to claim 1 or 2, wherein the iodine-containing inorganic material is at least one member selected from the group consisting of iodine, metal iodides, and iodine-containing interhalogen compounds.

10

[Claim 4]

A method for producing a perfluoroalkyne compound represented by formula (1A):

15 $R^1C \equiv CR^2$ (1A)

wherein

R^1 and R^2 are the same or different, and each represents a fluorine atom or a perfluoroalkyl group,

the method comprising the step of reacting a halogenated alkene compound represented by formula (2A):

20

$X^1R^1C=CR^2X^2$ (2A)

wherein

R^1 and R^2 are as defined above, and

X^1 and X^2 are the same or different, and each represents a halogen atom,

25

in at least one nitrogen-containing polar organic solvent selected from the group consisting of N,N-dimethylacetamide, N,N-diisopropylformamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidinone, triamide hexamethylphosphate, amine compounds, pyridine compounds, and quinoline compounds in the presence of zinc or zinc alloy, to obtain a perfluoroalkyne compound represented by formula (1A).

30

[Claim 5]

The production method according to any one of claims 1

35

to 4, wherein the reaction temperature is 0 to 250°C.

[Claim 6]

A composition comprising:

5 a perfluoroalkyne compound represented by formula (1A):



wherein

R^1 and R^2 are the same or different, and each represents a fluorine atom or a perfluoroalkyl group, and

10 a compound represented by formula (3):



wherein

R^1 and R^2 are as defined above.

15 [Claim 7]

The composition according to claim 6, wherein the amount of the perfluoroalkyne compound represented by formula (1A) is 85 to 99.9 mol% based on the total amount of the composition defined as 100 mol%.

20

[Claim 8]

The composition according to claim 6 or 7, which is used as a cleaning gas, an etching gas, or a building block for organic synthesis.

25