

DESCRIPTION

Title of Invention: CYCLOBUTENE PRODUCTION METHOD

Technical Field

5 [0001]

The present disclosure relates to a method for producing cyclobutene.

Background Art

10 [0002]

Cyclobutenes that contain halogen atoms are useful compounds, for example, in various refrigerants, foaming agents, and heat transfer mediums, as well as dry etching gas for semiconductors.

15 [0003]

Of cyclobutenes that contain halogen atoms, 1H-pentafluorocyclobutene is known to be produced from 1H,2H-hexafluorocyclobutane by a method performing a dehydrofluorination reaction (e.g., Non-patent Literature 1 and 2). This technique synthesizes 1H-pentafluorocyclobutene in an open reaction system by using a glass instrument.

Citation List

Non-patent Literature

25 [0004]

NPL 1: Buxton, Tatlow, Journal of the Chemical Society, (1954), pp. 1177-1179

NPL 2: Fuller, G., Tatlow, J. C., Journal of the Chemical Society, (1961), pp. 3198-3203

30

Summary of Invention

Technical Problem

[0005]

An object of the present disclosure is to produce a halogen atom-containing cyclobutene at a high conversion rate

35

(yield) and a high selectivity.

Solution to Problem

[0006]

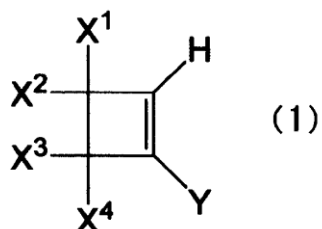
5 The present disclosure includes the following subject matter.

[0007]

Item 1.

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

[0008]

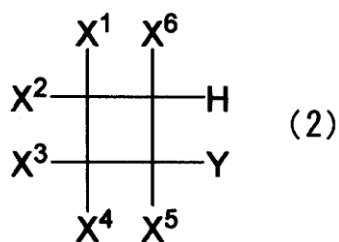


[0009]

15 wherein X¹, X², X³, and X⁴ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, and Y represents a halogen atom,

[0010]

20 the method comprising subjecting to an elimination reaction a cyclobutane represented by formula (2):



[0011]

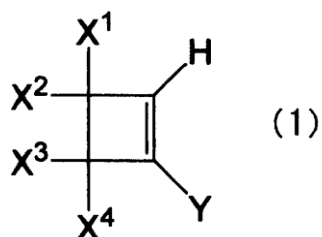
25 wherein X¹, X², X³, X⁴, and Y are as defined above, X⁵ and X⁶ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, wherein the elimination reaction is performed in the presence of a base in a closed reaction system.

[0012]

Item 2.

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

5 [0013]

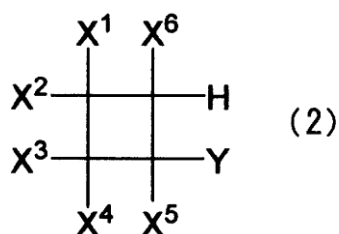


[0014]

wherein X^1 , X^2 , X^3 , and X^4 are the same or different and represent a hydrogen atom, a halogen atom, or a
10 perfluoroalkyl group, and Y represents a halogen atom,

the method comprising subjecting to an elimination reaction a cyclobutane represented by formula (2):

[0015]



15

[0016]

wherein X^1 , X^2 , X^3 , X^4 , and Y are as defined above, and X^5 and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group,
20 wherein the elimination reaction is performed at a reaction temperature of 20°C or more under a reaction pressure of 0 kPa or more in the presence of a base.

[0017]

Item 3.

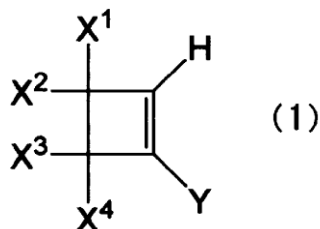
25 The method according to Item 1 or 2, wherein X^5 represents a hydrogen atom, X^6 represents a halogen atom, and the elimination reaction is a dehydrohalogenation reaction.

[0018]

Item 4.

A composition comprising a cyclobutene represented by formula (1):

5 [0019]



[0020]

wherein X^1 , X^2 , X^3 , and X^4 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, and Y represents a halogen atom,

10 wherein the cyclobutene represented by formula (1) is present in an amount of 99 mol% or more based on the total amount of the composition taken as 100 mol%.

[0021]

15 Item 5.

The composition according to Item 4, wherein 1H-perfluorocyclobutene (1H- $\text{C}_4\text{F}_5\text{H}$) is present in an amount of 99 mol% or more, and 3H-perfluorocyclobutene (3H- $\text{C}_4\text{F}_5\text{H}$) is present in an amount of 1 mol% or less.

20 [0022]

Item 6.

The composition according to Item 4 or 5, which is for use in cleaning gas, etching gas, deposit gas, or a building block for organic synthesis.

25

Advantageous Effects of Invention

[0023]

The present disclosure enables the production of a halogen atom-containing cyclobutene at a high conversion rate

30 (yield) and a high selectivity.

Description of Embodiments

[0024]

The present inventors conducted extensive research and found that a halogen atom-containing cyclobutene represented by
5 formula (1) can be produced at a high conversion rate (yield) and a high selectivity by performing an elimination reaction on a starting material compound in the presence of a base in a closed reaction system.

[0025]

10 The inventors conducted further research on the basis of the finding and completed the present disclosure.

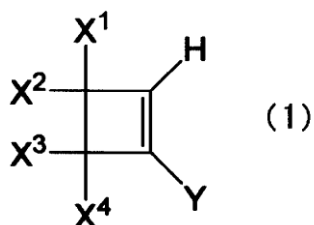
[0026]

The present disclosure includes the following embodiment.

15 [0027]

The method according to the present disclosure for producing a cyclobutene represented by formula (1):

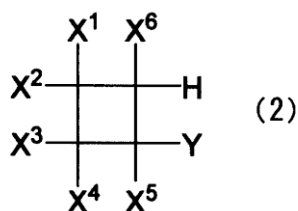
[0028]



20 [0029]

wherein X¹, X², X³, and X⁴ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, and Y represents a halogen atom comprising subjecting to an elimination reaction a cyclobutane represented by formula (2):

25 [0030]



[0031]

wherein X¹, X², X³, X⁴, and Y are as defined above, X⁵ and X⁶ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group.

[0032]

5 In present disclosure, the step of the elimination reaction is performed in the presence of a base in a closed reaction system.

[0033]

10 In present disclosure, the step of the elimination reaction is performed at a reaction temperature of 20°C or more under a reaction pressure of 0 kPa or more in the presence of a base.

[0034]

15 In present disclosure, the reaction pressure is a gauge pressure unless indicated otherwise.

[0035]

20 In present disclosure, a halogen atom-containing cyclobutene can be produced at a high conversion rate (yield) and a high selectivity by satisfying the requirements described above.

[0036]

25 In the present disclosure, "conversion rate" refers to the percentage (mol%) of the total molar quantity of the compounds (e.g., a halogen atom-containing cyclobutene) other than the starting material compound present in a gas flowing out from a reactor outlet relative to the molar quantity of the starting material compound (a halogen atom-containing cyclobutane) supplied to a reactor.

[0037]

30 In the present disclosure, "selectivity" refers to the percentage (mol%) of the total molar quantity of the target compound (a halogen atom-containing cyclobutene) present in a gas flowing out from a reactor outlet relative to the total molar quantity of the compounds other than the starting material
35 compound (e.g., a halogen atom-containing cyclobutene) in the gas

flowing out from the reactor outlet.

[0038]

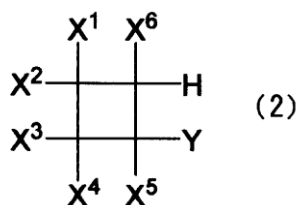
The method for producing a cyclobutene according to present disclosure can increase the yield of the target compound by applying pressure to increase the boiling point of the starting material by using, for example, a metal container, unlike the reaction using a glass container in the prior art, in order to increase the liquid component.

[0039]

10 (1) Starting Material Compound

In the present disclosure, the starting material compound is a cyclobutane represented by formula (2):

[0040]



15 [0041]

wherein X¹, X², X³, X⁴, X⁵, and X⁶ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, and Y represents a halogen atom.

[0042]

20 X¹, X², X³, X⁴, X⁵, and X⁶ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group.

[0043]

Y represents a halogen atom.

25 [0044]

The halogen atom represented by X¹, X², X³, X⁴, X⁵, X⁶, and Y includes a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

[0045]

30 The perfluoroalkyl group represented by X¹, X², X³, X⁴, X⁵, and X⁶ is an alkyl group in which all of the hydrogen atoms are replaced with a fluorine atom. The perfluoroalkyl group has,

for example, 1 to 20 carbon atoms, preferably 1 to 12 carbon atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and particularly preferably 1 to 3 carbon atoms. The perfluoroalkyl group is preferably a linear or
 5 branched perfluoroalkyl group. The perfluoroalkyl group is preferably a trifluoromethyl group (CF₃-) or a pentafluoroethyl group (C₂F₅-).

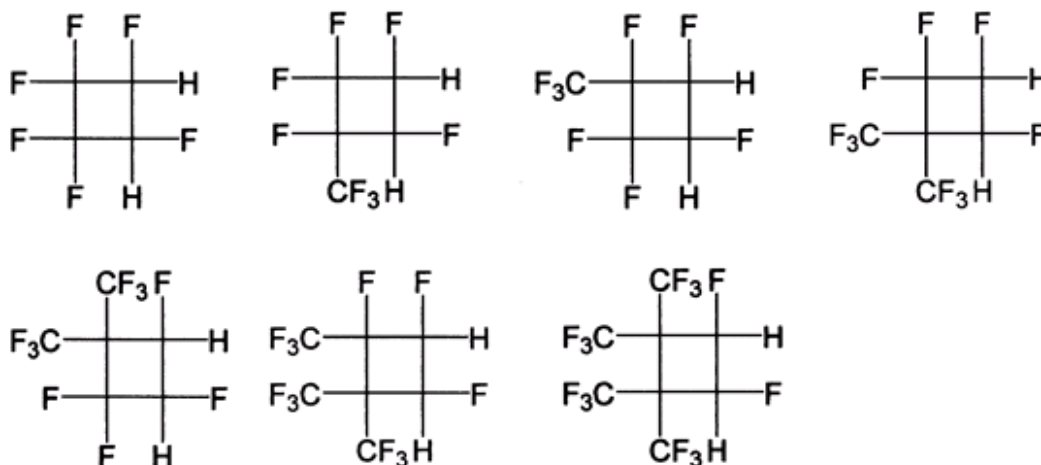
[0046]

From the standpoint of producing a halogen atom-
 10 containing cyclobutene at a high selectivity, the halogen atom- containing cyclobutane represented by formula (2), which is a starting material compound, is more preferably a cyclobutane wherein X¹, X², X³, and X⁴ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, X⁵
 15 represents a hydrogen atom, X⁶ represents a fluorine atom, and Y represents a fluorine atom.

[0047]

Examples of the cyclobutane represented by formula (2), which is a starting material compound, include the following
 20 compounds.

[0048]



[0049]

[0050]

25 These cyclobutanes represented by formula (2) may be used singly or in a combination of two or more. These

cyclobutanes for use may be known compounds or commercially available products.

[0051]

From the standpoint of producing a halogen atom-
5 containing cyclobutene at a high selectivity and a high conversion rate (yield), the halogen atom-containing cyclobutane represented by formula (2) is more preferably a cyclobutane wherein X¹, X², X³, X⁴, and X⁶ represent a fluorine atom, X⁵ represents a hydrogen atom, and Y represents a fluorine atom.

10 [0052]

(2) Elimination Reaction

The method for producing a halogen atom-containing cyclobutene according to the present disclosure first prepares a solution of the starting material compound represented by formula
15 (2).

[0053]

In the elimination reaction step of the present disclosure, an elimination reaction is performed in the presence of a base in a closed reaction system.

20 [0054]

In the elimination reaction step of the present disclosure, it is preferred that X⁵ be a hydrogen atom, X⁶ be a halogen atom, and the elimination reaction be a dehydrohalogenation reaction. In the elimination reaction step of
25 the present disclosure, it is preferred that X⁵ be a hydrogen atom, X⁶ be a fluorine atom, and the elimination reaction be a dehydrofluorination reaction.

[0055]

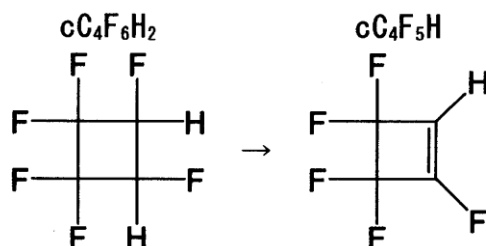
For example, the halogen atom-containing cyclobutane
30 represented by formula (2) as a starting material compound is preferably a cyclobutane wherein X¹, X², X³, X⁴, and X⁶ are a fluorine atom, X⁵ is a hydrogen atom, and Y is a fluorine atom.

[0056]

In accordance with the following reaction scheme, the
35 elimination reaction is preferably a dehydrofluorination

reaction.

[0057]



[0058]

5 Solvent

The solvent is preferably water. Preferable non-aqueous solvents include ester carbonates, such as dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, and ethyl propyl carbonate; esters, such as ethyl acetate, propyl acetate, butyl acetate, methyl propionate, ethyl propionate, and butyl propionate; ketones, such as acetone, ethyl methyl ketone, and diethyl ketone; lactones, such as γ -butyrolactone, γ -valerolactone, tetrahydrofuran, and tetrahydropyran; ethers, such as diethyl ether, dibutyl ether, diisopropyl ether, 1,2-dimethoxyethane, 1,2-diethoxyethane, and tetrahydrofuran; nitriles, such as acetonitrile, propionitrile, and benzonitrile; amides, such as N,N-dimethylformamide; and sulfones, such as dimethyl sulfoxide and sulfolane. The solvent is preferably at least one member selected from the group consisting of water and these non-aqueous solvents.

[0059]

Base

In this step, the base for use is preferably an alkali.

[0060]

The alkali for use in this step is preferably a hydroxide of an alkali metal or alkali earth metal, and more preferably sodium hydroxide or potassium hydroxide. In this step, the alkali for use is preferably an aqueous solution of a hydroxide of an alkali metal or alkali earth metal, and particularly more preferably an aqueous solution of sodium hydroxide or potassium hydroxide. The use of such an alkali

enables the production of the target compound at a higher selectivity and a higher conversion rate.

[0061]

The hydroxide of an alkali metal or alkali earth metal
5 in the reaction solution, preferably in an aqueous solution, can be of any amount. The amount of the hydroxide of an alkali metal or alkali earth metal is preferably 20 to 60 mass%, and more preferably 40 to 55 mass% based on the total amount of the reaction solution. An amount of the alkali in the reaction
10 solution within these ranges enables the production of the target compound at a higher selectivity and a higher conversion rate.

[0062]

In this step, the base for use is preferably an alkoxide of an organic substance. Examples of alkoxides of an
15 organic substance preferable for use include methoxy potassium, ethoxy potassium, and t-butoxy potassium.

[0063]

Catalyst

In this step, a catalyst can be optionally used. The
20 catalyst for use in this step is preferably a hydrocarbon-based alkoxide. The hydrocarbon-based alkoxide is preferably at least one member selected from the group consisting of tetramethylammonium fluoride, tetramethylammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide,
25 tetraethylammonium fluoride, tetraethylammonium chloride, tetraethylammonium bromide, tetraethylammonium iodide, tetrapropylammonium fluoride, tetrapropylammonium chloride, tetrapropylammonium bromide, tetrapropylammonium iodide, tetrabutylammonium fluoride, tetrabutylammonium chloride,
30 tetrabutylammonium bromide, tetrabutylammonium iodide, benzyltriethylammonium fluoride, benzyltriethylammonium chloride, benzyltriethylammonium bromide, benzyltriethylammonium iodide, benzyltributylammonium fluoride, benzyltributylammonium chloride, benzyltributylammonium bromide, benzyltributylammonium iodide,
35 methyltributylammonium fluoride, methyltributylammonium chloride,

methyltributylammonium bromide, methyltributylammonium iodide, methyltrioctylammonium fluoride, methyltrioctylammonium chloride (trademark: Aliquat336), methyltrioctylammonium bromide, and methyltrioctylammonium iodide. The use of such a catalyst enables
5 the production of the target compound at a higher selectivity and a higher conversion rate.

[0064]

Closed Reaction System

A feature of the elimination reaction step of the
10 present disclosure is that the elimination reaction is performed in the presence of the base described above in a closed reaction system.

[0065]

The halogen atom-containing cyclobutene represented by
15 formula (1), which is the target compound of the present disclosure, has a low boiling point and is a gas at room temperature. Thus, forming a reaction system into a closed reaction system in the elimination reaction step of the present disclosure naturally increases the pressure inside the closed
20 reaction system. This leads the reaction to proceed under increased pressure.

[0066]

The low boiling point of the target compound increases the pressure in the closed reaction system and increases the
25 concentration of the substrate (starting material compound) in the reaction solution (base solution), thus improving reactivity. It is preferred that the closed reaction system be prepared by closing a reaction system by using a batch-mode pressure-resistant reactor to perform a reaction. In performing a reaction
30 in batch mode, for example, it is preferred that the starting material compound, the base solution (alkali aqueous solution), the catalyst, and other components be placed in a pressure container such as an autoclave, heated to a proper reaction temperature with a heater, and allowed to react with stirring for
35 a predetermined time period. The reaction is preferably performed

in an atmosphere of inert gas, such as nitrogen, helium, or carbon dioxide gas.

[0067]

5 In the elimination reaction step of the present disclosure, the lower limit of the reaction temperature of the closed reaction system is typically 20°C, preferably 25°C, more preferably 30°C, and still more preferably 40°C from the standpoint of more efficiently performing the elimination reaction to obtain the target compound at a higher selectivity
10 and suppressing a decrease in the conversion rate.

[0068]

In the elimination reaction step of the present disclosure, the upper limit of the reaction temperature of the closed reaction system is typically 50°C and preferably 45°C from
15 the standpoint of more efficiently performing the dehydrofluorination reaction to obtain the target compound at a higher selectivity and suppressing a decrease in the selectivity due to decomposition or polymerization of the reaction product.

[0069]

20 In the elimination reaction step of the present disclosure, the target compound can be obtained at a higher selectivity and a higher conversion rate by performing the reaction in a closed reaction system.

[0070]

25 Pressure-Increased Reaction System

A feature of the elimination reaction step of the present disclosure is that the elimination reaction is performed at a reaction temperature of 20°C or more under a reaction pressure of 0 kPa or more in the presence of the base described
30 above.

[0071]

Increasing the pressure in the reaction system increases the concentration of the substrate (starting material compound) in the reaction solution (base solution, alkali aqueous
35 solution), thus improving reactivity. The reaction in the

pressure-increased reaction system is preferably performed by using a batch-mode pressure-resistant reactor with the reaction system closed. In performing a reaction in batch mode, for example, it is preferred that the starting material compound, the
5 base solution (alkali aqueous solution), the catalyst, and other components be placed in a pressure container such as an autoclave, heated to a proper reaction temperature with a heater, and allowed to react with stirring for a predetermined time period.

10 [0072]

In the elimination reaction step of the present disclosure, the reaction pressure is 0 kPa or more as a pressure-increasing condition.

[0073]

15 The reaction pressure refers to the pressure inside the reactor used for the pressure-increased reaction system. In the elimination reaction step of the present disclosure, the reaction is performed under a reaction pressure of preferably 0 kPa or more, more preferably 10 kPa or more, still more preferably 20
20 kPa or more, and particularly preferably 30 kPa or more.

[0074]

In the elimination reaction step of the present disclosure, as a pressure-increasing condition, the reaction is performed under an absolute pressure of preferably 101.3 kPa or
25 more, more preferably 111.3 kPa or more, still more preferably 121.3 kPa or more, and particularly preferably 131.3 kPa or more.

[0075]

The pressure in the reaction system can be increased by sending inert gas, such as nitrogen, helium, or carbon dioxide
30 gas, into the reaction system.

[0076]

In the elimination reaction step of the present disclosure, the lower limit of the reaction temperature of the pressure-increased reaction system is typically 20°C, preferably
35 25°C, more preferably 30°C, and still more preferably 40°C from

the standpoint of efficiently performing the elimination reaction to obtain the target compound at a higher selectivity and suppressing a decrease in the conversion rate.

[0077]

5 In the elimination reaction step of the present disclosure, the lower limit of the reaction temperature of the pressure-increased reaction system is typically 20°C in order to adjust the reaction pressure to 0 kPa or more or the absolute pressure to 101.3 kPa or more as a pressure-increasing condition.
10 In the elimination reaction step of the present disclosure, it is preferable to perform an elimination reaction by heating the inside of the reactor and increasing the pressure of the inside of the reactor.

[0078]

15 In the elimination reaction step of the present disclosure, the upper limit of the reaction temperature of the pressure-increased reaction system is typically 50°C and preferably 45°C from the standpoint of more efficiently performing the dehydrofluorination reaction to obtain the target
20 compound at a higher selectivity and suppressing a decrease in selectivity due to decomposition or polymerization of the reaction product.

[0079]

 In the elimination reaction step of the present
25 disclosure, the target compound can be obtained at a higher selectivity and a higher conversion rate by performing the reaction in a pressure-increased reaction system.

[0080]

 After completion of the elimination reaction, a
30 purification treatment can be optionally performed in accordance with an ordinary method to obtain a halogen atom-containing cyclobutene represented by formula (1).

[0081]

Combination of Closed Reaction System with Pressure-Increased
35 Reaction System

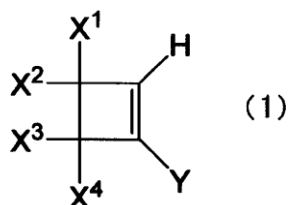
In the elimination reaction step of the present disclosure, the reaction may be performed in a continuous and pressure-increasing mode, while taking out the liquid or the reaction product formed into a gas, by using a continuous stirred-tank reactor (CSTR) to which a back pressure valve is attached.

[0082]

(3) Target Compound

The target compound according to the present disclosure is a halogen atom-containing cyclobutene represented by formula (1):

[0083]



[0084]

wherein X^1 , X^2 , X^3 , and X^4 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, and Y represents a halogen atom.

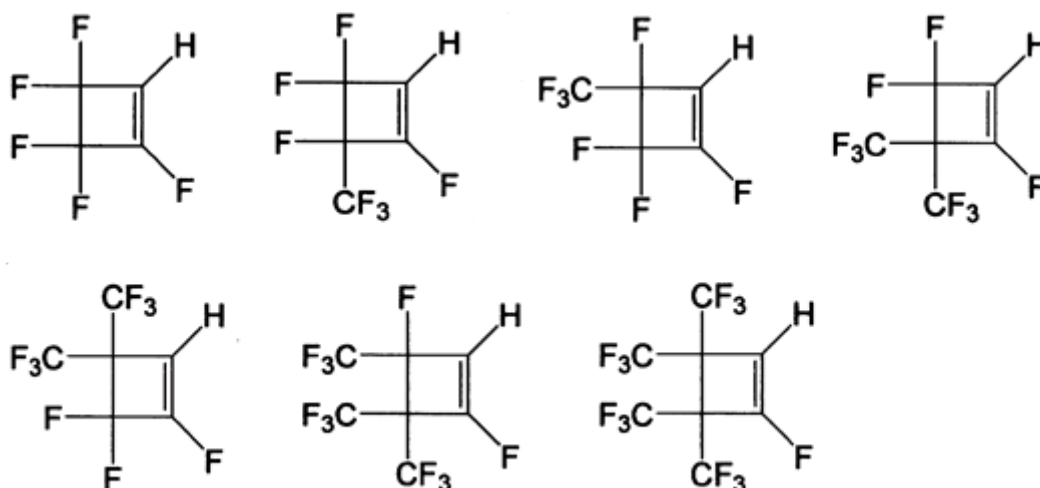
[0085]

X^1 , X^2 , X^3 , X^4 , and Y are as defined above.

[0086]

Examples of the cyclobutene represented by formula (1) to be produced include the following.

[0087]



[0088]

[0089]

The halogen atom-containing cyclobutene represented by
 5 formula (1) is preferably a cyclobutene wherein X^1 , X^2 , X^3 , and X^4
 are the same or different and represent a hydrogen atom, a
 halogen atom, or a perfluoroalkyl group, and Y is a fluorine
 atom. The halogen atom-containing cyclobutene represented by
 formula (1) is more preferably a cyclobutene wherein X^1 , X^2 , X^3 ,
 10 and X^4 are a fluorine atom, and Y is a fluorine atom.

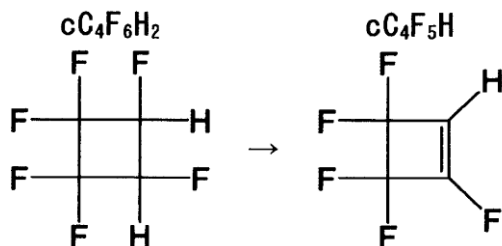
[0090]

In the method for producing a halogen atom-containing
 cyclobutene according to present disclosure, the starting
 material compound for use in the elimination reaction is
 15 preferably a halogen atom-containing cyclobutane represented by
 formula (2) wherein X^1 , X^2 , X^3 , X^4 , and X^6 are a fluorine atom, X^5
 is a hydrogen atom, and Y is a fluorine atom.

[0091]

In accordance with the following reaction scheme, the
 20 elimination reaction is preferably a dehydrofluorination
 reaction.

[0092]



[0093]

The target compound is preferably a halogen atom-
 5 containing cyclobutene represented by formula (1) wherein X^1 , X^2 , X^3 , and X^4 are a fluorine atom, and Y is a fluorine atom.

[0094]

(4) Composition Containing Halogen Atom-Containing Cyclobutene

In the manner described above, a halogen atom-
 10 containing cyclobutene represented by formula (1) can be obtained. However, as described above, a halogen atom-containing cyclobutene represented by formula (1) may also be obtained in the form of a composition containing a halogen atom-containing cyclobutene represented by formula (1) and a halogen atom-
 15 containing cyclobutane represented by formula (2).

[0095]

The halogen atom-containing cyclobutene represented by
 formula (1) contained in such a composition is preferably a
 cyclobutene wherein X^1 , X^2 , X^3 , and X^4 are a fluorine atom, and Y
 20 is a fluorine atom.

[0096]

In the composition containing the halogen atom-
 containing cyclobutene represented by formula (1) according to
 present disclosure, the halogen atom-containing cyclobutene
 25 represented by formula (1) is preferably present in an amount of 99 mol% or more based on the total amount of the composition taken as 100 mol%.

[0097]

In the composition containing the halogen atom-
 30 containing cyclobutene represented by formula (1) according to present disclosure, the halogen atom-containing cyclobutene

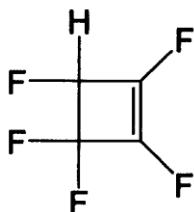
represented by formula (1) is preferably present in an amount of 1 mol% to 99.9mol%, more preferably 5 mol% to 99.9 mol%, and still more preferably 10 mol% to 99.9 mol% based on the total amount of the composition taken as 100 mol%.

5 [0098]

The method for producing a halogen atom-containing cyclobutene according to the present disclosure may produce the following compound as impurities in the elimination reaction described above.

10 [0099]

cC₄F₅H (3H-cC₄F₅H)



[0100]

In the composition containing the halogen atom-containing cyclobutene represented by formula (1) according to the present disclosure, it is preferred that 1H-perfluorocyclobutene (1H-cC₄F₅H) be present in an amount of 99 mol% or more, and 3H-perfluorocyclobutene (3H-cC₄F₅H) be present in an amount of 1 mol% or less based on the total amount of the composition taken as 100 mol%.

20

[0101]

The production method according to present disclosure produces the halogen atom-containing cyclobutene represented by formula (1) particularly at a high selectivity even when the halogen atom-containing cyclobutene represented by formula (1) is obtained in the form of a composition containing such a cyclobutene. Thus, it is possible to reduce the components other than the halogen atom-containing cyclobutene represented by formula (1) in the composition. The production method according to the present disclosure can reduce labor for performing purification to obtain the halogen atom-containing cyclobutene

30

represented by formula (1).

[0102]

The composition containing the halogen atom-containing cyclobutene represented by formula (1) according to the present disclosure can be used effectively in a variety of areas, such as for etching gas for forming state-of-the-art microstructures, such as semiconductors and liquid crystals, as well as deposit gas, building blocks for organic synthesis, and cleaning gas, in the same manner as with the halogen atom-containing cyclobutene represented by formula (1) alone.

[0103]

The deposit gas refers to a gas for depositing an etching-resistant polymer layer.

[0104]

The building blocks for organic synthesis refer to a substance that can serve as a precursor of a compound that has a highly reactive skeleton. For example, reacting the halogen atom-containing cyclobutene represented by formula (1) according to present disclosure or the composition containing the halogen atom-containing cyclobutene with a fluorine-containing organic silicon compound such as $\text{CF}_3\text{Si}(\text{CH}_3)_3$ introduces a fluoroalkyl group such as a CF_3 group, and this converts the cyclobutene or the composition into a substance that can be used as a cleaner or a fluorine-containing pharmaceutical intermediate.

[0105]

The above describes embodiments of the present disclosure. However, various modifications may be made on the embodiments and details without departing from the spirit and principal concept of the claims.

30

Examples

[0106]

The following describes the present disclosure in more detail with reference to Examples. However, the present disclosure is not limited to these Examples.

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[0107]

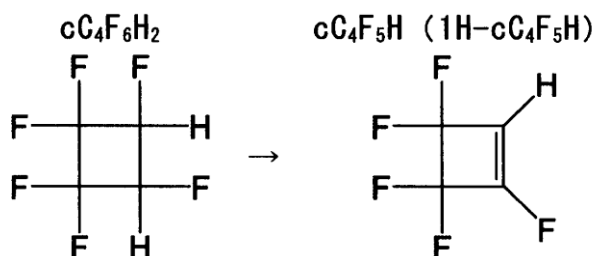
Example

In the Examples, the method for producing a halogen atom-containing cyclobutene used a halogen atom-containing cyclobutane represented by formula (2) wherein X^1 , X^2 , X^3 , X^4 , and X^6 are a fluorine atom, X^5 is a hydrogen atom, and Y is a fluorine atom as a starting material compound.

[0108]

In accordance with the following reaction scheme, the elimination reaction was a dehydrofluorination reaction.

[0109]



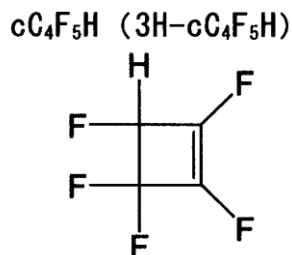
[0110]

The target compound was a halogen atom-containing cyclobutene represented by formula (1) wherein X^1 , X^2 , X^3 , and X^4 are a fluorine atom, and Y is a fluorine atom.

[0111]

In the elimination reaction described above, the following compound can be produced as impurities.

[0112]



[0113]

Example

The reaction system for use was an autoclave (200 cc).

[0114]

Due to the use of an autoclave as a reaction system, this reaction system shows (i) an embodiment of a closed reaction system in which a reaction is performed in the presence of a base (alkali) and (ii) an embodiment of a pressure-increased reaction system in which a reaction is performed at a reaction temperature of 20°C or more under a reaction pressure of 0 kPa or more in the presence of a base (alkali). As in this manner, sealing is involved when pressure is increased.

[0115]

Example 1

A 50 wt% aqueous KOH solution as a reaction solution and a starting material compound ($\text{C}_4\text{F}_6\text{H}_2$) were added to an autoclave and sealed with a lid to form a closed system, followed by sending nitrogen to apply pressure. The pressure at this time was 20 kPa. Thereafter, the mixture was stirred at room temperature (25°C) to allow a reaction to proceed. After the start of a dehydrofluorination reaction, sampling was performed. When no change was observed in the formulation of the reaction system, the reaction was ended. The pressure at the end of the reaction was 80 kPa.

[0116]

After stirring the reaction mixture was ended, the reaction mixture was cooled to 0°C. Mass spectrometry was performed by gas chromatography (trade name: GC-2014, produced by Shimadzu Corporation) in accordance with gas chromatography-mass spectrometry (GC-MS), and structural analysis based on an NMR spectrum was performed by using an NMR spectrometer (trade name: 400YH, produced by JEOL).

[0117]

The results of the mass spectrometry and structural analysis indicated that $\text{C}_4\text{F}_5\text{H}$ was formed as a target compound. In Example 1, the conversion rate from $\text{C}_4\text{F}_6\text{H}_2$ (starting material compound) was 92.1 mol%, and the selectivity (yield) for $\text{C}_4\text{F}_5\text{H}$ (target compound) was 97.8 mol%.

[0118]

Example 2

In accordance with the experimental method of Example 1, a dehydrofluorination reaction was started by using methyltrioctylammonium chloride (trademark: Aliquat336) as a catalyst. The dehydrofluorination reaction, mass spectrometry, and structural analysis were performed in the same manner as in Example 1 except for this condition.

[0119]

The results of the mass spectrometry and structural analysis indicated that $\text{C}_4\text{F}_5\text{H}$ was formed as a target compound. In Example 2, the conversion rate from $\text{C}_4\text{F}_6\text{H}_2$ (starting material compound) was 93.2 mol%, and the selectivity for $\text{C}_4\text{F}_5\text{H}$ (target compound) was 98.9 mol%.

[0120]

Example 3

In accordance with the experimental method of Example 1, a dehydrofluorination reaction was started by using a 50 wt% solution of KOH in dibutyl ether prepared by adding KOH (alkali) as a base to dibutyl ether (reaction solvent) as a reaction solution. The dehydrofluorination reaction, mass spectrometry, and structural analysis were performed in the same manner as in Example 1 except for this condition.

[0121]

The results of mass spectrometry and structural analysis indicated that $\text{C}_4\text{F}_5\text{H}$ was formed as a target compound. In Example 3, the conversion rate from $\text{C}_4\text{F}_6\text{H}_2$ (starting material compound) was 93.4 mol%, and the selectivity for $\text{C}_4\text{F}_5\text{H}$ (target compound) was 98.5 mol%.

[0122]

Example 4

In accordance with the experimental method of Example 1, a dehydrofluorination reaction was started by using a dibutyl ether solution prepared by adding tert-butoxypotassium (t-BuOK) as a base (1.2 equivalent amount) to a dibutyl ether (reaction

solvent) as a reaction solution. The dehydrofluorination reaction, mass spectrometry, and structural analysis were performed in the same manner as in Example 1 except for this condition.

5 [0123]

The results of mass spectrometry and structural analysis indicated that $\text{cC}_4\text{F}_5\text{H}$ was formed as a target compound. In Example 3, the conversion rate from $\text{cC}_4\text{F}_6\text{H}_2$ (starting material compound) was 95.4 mol%, and the selectivity for $\text{cC}_4\text{F}_5\text{H}$ (target compound) was 98.9 mol%.

10 [0124]

Comparative Example 1

In Comparative Example 1, an open reaction system was used. 50 wt% KOH was added to a flask (200 cc), and a dry ice
15 condenser and a dropping funnel were attached to the flask. A starting material compound ($\text{cC}_4\text{F}_6\text{H}_2$) was placed in the dropping funnel to perform dropwise addition. Thereafter, the mixture was stirred at room temperature. After the start of a dehydrofluorination reaction, sampling was performed. When no
20 change was observed in the formulation of the reaction system, the reaction was ended. The reaction was performed in an open system, and the pressure was constantly 0 kPa.

[0125]

After stirring the reaction mixture was ended, the
25 reaction mixture was cooled to 0°C. The results of mass spectrometry and structural analysis indicated that $\text{cC}_4\text{F}_5\text{H}$ was formed as a target compound. In Comparative Example 1, the conversion rate from $\text{cC}_4\text{F}_6\text{H}_2$ (starting material compound) was 51.7 mol%, and the selectivity for $\text{cC}_4\text{F}_5\text{H}$ (target compound) was 97.1
30 mol%.

[0126]

Table 1

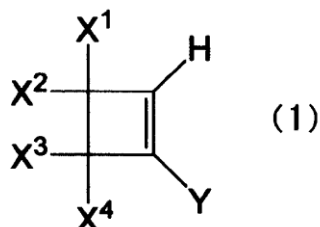
	Reaction System	Solvent	Type of Catalyst	Reaction Temperature (°C)	Reaction Time (hr)	Conversion Rate from Starting Material Compound cC4F6H2 (mol%)	Selectivity for Target Compound 1H-cC4F5H (mol%)	Selectivity for 3H-cC4F5H (mol%)	Other Generated Products (mol%)
Example 1	Closed and Pressure-Increased Reaction System	Water	No Catalyst Added	25	5	92.1	97.8	0.2	2.0
Example 2	Closed and Pressure-Increased Reaction System	Water	Methyltriethylammonium Chloride	25	2	93.2	98.9	0.1	1.0
Example 3	Closed and Pressure-Increased Reaction System	Dibutyl Ether (KOH Contained)	No Catalyst Added	25	2	93.4	98.5	0.2	1.3
Example 4	Closed and Pressure-Increased Reaction System	Dibutyl Ether (t-BuOK Contained)	No Catalyst Added	25	2	95.4	98.9	0.2	0.9
Comparative Example 1	Open Reaction System	Water	No Catalyst Added	25	5	51.7	97.1	0.1	2.8

CLAIMS

[Claim 1]

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

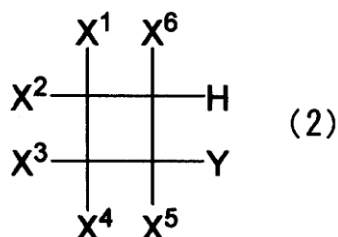
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wherein X^1 , X^2 , X^3 , and X^4 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, and Y represents a halogen atom,

10

the method comprising subjecting to an elimination reaction a cyclobutane represented by formula (2):



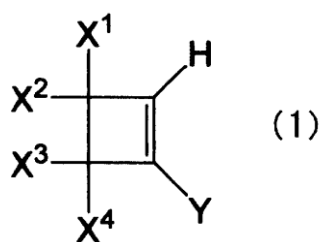
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wherein X^1 , X^2 , X^3 , X^4 , and Y are as defined above, X^5 and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, wherein the elimination reaction is performed in the presence of a base in a closed reaction system.

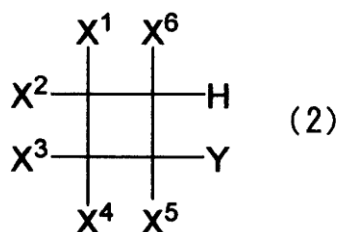
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[Claim 2]

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



wherein X^1 , X^2 , X^3 , and X^4 are the same or different and represent a hydrogen atom, a halogen atom, or a
 5 perfluoroalkyl group, and Y represents a halogen atom,
 the method comprising subjecting to an elimination
 reaction a cyclobutane represented by formula (2):



10

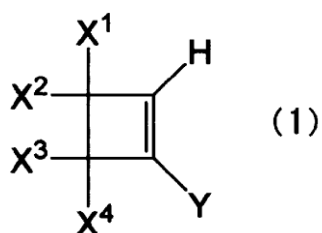
wherein X^1 , X^2 , X^3 , X^4 , and Y are as defined above,
 and X^5 and X^6 are the same or different and represent a hydrogen
 atom, a halogen atom, or a perfluoroalkyl group,
 wherein the elimination reaction is performed at a reaction
 15 temperature of 20°C or more under a reaction pressure of 0 kPa or
 more in the presence of a base.

[Claim 3]

The method according to claim 1 or 2, wherein X^5
 20 represents a hydrogen atom, X^6 represents a halogen atom, and the
 elimination reaction is a dehydrohalogenation reaction.

[Claim 4]

A composition comprising a cyclobutene represented by
 25 formula (1):



wherein X^1 , X^2 , X^3 , and X^4 are the same or different and represent a hydrogen atom, a halogen atom, or a
5 perfluoroalkyl group, and Y represents a halogen atom,
wherein the cyclobutene represented by formula (1) is present in
an amount of 99 mol% or more based on the total amount of the
composition taken as 100 mol%.

10 [Claim 5]

The composition according to claim 4, wherein 1H-perfluorocyclobutene ($1H-C_4F_5H$) is present in an amount of 99 mol% or more, and 3H-perfluorocyclobutene ($3H-C_4F_5H$) is present
in an amount of 1 mol% or less.

15

[Claim 6]

The composition according to claim 4 or 5, which is for
use in cleaning gas, etching gas, deposit gas, or a building
block for organic synthesis.

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