

DESCRIPTION

Title of Invention: METHOD FOR PRODUCING CYCLOBUTENE

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

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Summary of Invention

Technical Problem

[0005]

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

35

Solution to Problem

[0006]

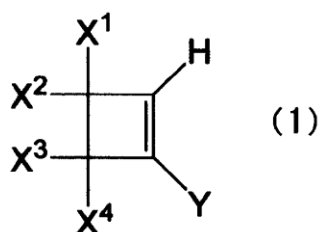
The present disclosure includes the following subject
5 matter.

[0007]

Item 1.

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

10 [0008]

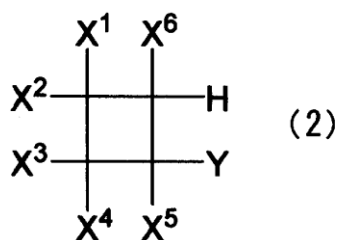


[0009]

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

[0010]

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



20

[0011]

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,
25 wherein the elimination reaction is performed in a gas phase.

[0012]

Item 2.

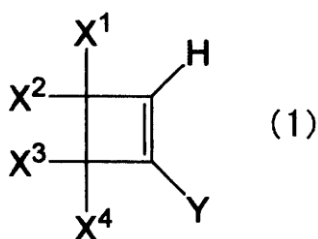
The method according to Item 1, wherein X^5 represents a hydrogen atom, X^6 represents a halogen atom, and the elimination reaction is a dehydrohalogenation reaction.

[0013]

5 Item 3.

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

[0014]



10 [0015]

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, wherein the cyclobutene represented by formula (1) is present in an amount of 95 mol% or more based on the total amount of the composition taken as 100 mol%.

[0016]

Item 4.

The composition according to Item 3, 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.

[0017]

Item 5.

25 The composition according to Item 3 or 4, which is for use in cleaning gas, etching gas, deposit gas, or a building block for organic synthesis.

Advantageous Effects of Invention

30 [0018]

The present disclosure enables the production of a

halogen atom-containing cyclobutene at a high selectivity.

Description of Embodiments

[0019]

5 The present inventors conducted extensive research and found that a halogen atom-containing cyclobutene represented by formula (1) can be produced at a high selectivity by performing an elimination reaction on a starting material compound in a gas phase.

10 [0020]

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

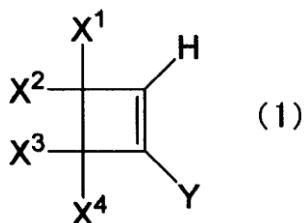
[0021]

15 The present disclosure includes the following embodiment.

[0022]

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

[0023]

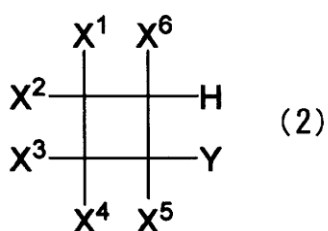


20

[0024]

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
25 represents a halogen atom comprises subjecting to an elimination reaction a cyclobutane represented by formula (2):

[0025]



[0026]

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

[0027]

In the present disclosure, the step of the elimination reaction is performed in a gas phase.

[0028]

In present disclosure, a halogen atom-containing cyclobutene can be produced at a high selectivity by satisfying the requirements described above.

[0029]

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 compound (e.g., a halogen atom-containing cyclobutene) in the gas flowing out from the reactor outlet.

[0030]

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

[0031]

The method for producing a cyclobutene according to the present disclosure uses a gas phase reaction of a circulating

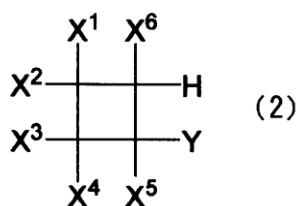
system rather than a batch reaction. Thus, the method according to the present disclosure is advantageous in the elimination of the need for a solvent and thus producing no industrial waste from the solvent.

5 [0032]

(1) Starting Material Compound

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

[0033]



10

[0034]

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.

15 [0035]

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

[0036]

20 Y represents a halogen atom.

[0037]

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.

25 [0038]

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

30

branched perfluoroalkyl group. The perfluoroalkyl group is preferably a trifluoromethyl group (CF_3-) or a pentafluoroethyl group (C_2F_5-).

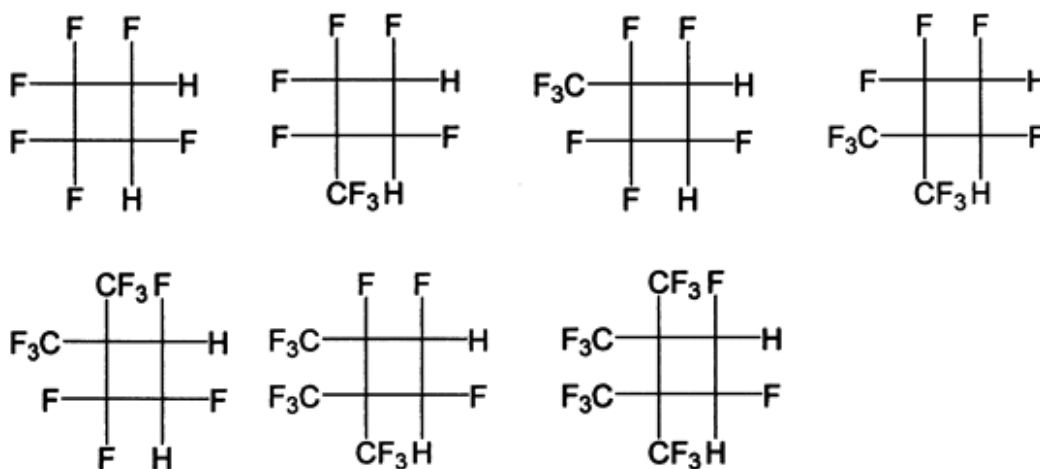
[0039]

5 From the standpoint of producing a halogen atom-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 X^1 , X^2 , X^3 , and X^4 are the same or different and represent
10 a hydrogen atom, a halogen atom, or a perfluoroalkyl group, X^5 represents a hydrogen atom, X^6 represents a fluorine atom, and Y represents a fluorine atom.

[0040]

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

[0041]



[0042]

20 [0043]

These cyclobutanes represented by formula (2) may be used singly or in a combination of two or more. These cyclobutanes for use may be commercially available products.

[0044]

25 From the standpoint of producing a halogen atom-containing cyclobutene at a high selectivity, the halogen atom-

containing cyclobutane represented by formula (2) is more preferably a cyclobutane wherein X^1 , X^2 , X^3 , X^4 , and X^6 represent a fluorine atom, X^5 represents a hydrogen atom, and Y represents a fluorine atom.

5 [0045]

(2) Elimination Reaction

In the elimination reaction step of the present disclosure, the elimination reaction is performed in a gas phase. In the elimination reaction step of the present disclosure, the
10 elimination reaction is preferably performed in a gas phase, in particular in gas-phase continuous flow mode using a fixed bed reactor. The elimination reaction performed in gas-phase continuous flow mode is advantageous because it can simplify the equipment, operation, etc., and it is also economical.

15 [0046]

In the elimination reaction step of the present disclosure, it is preferred that X^5 be a hydrogen atom, X^6 be a halogen atom, and the elimination reaction be a dehydrohalogenation reaction. In the elimination reaction step of
20 the present disclosure, it is preferred that X^5 be a hydrogen atom, X^6 be a fluorine atom, and the elimination reaction be a dehydrofluorination reaction.

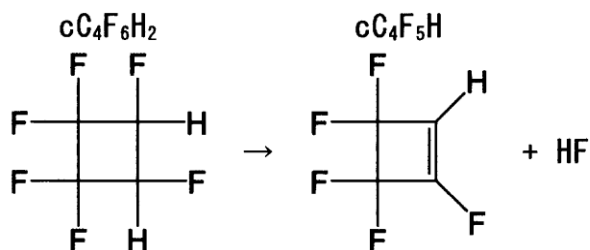
[0047]

For example, the halogen atom-containing cyclobutane
25 represented by formula (2) as a starting material compound is preferably a cyclobutane 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.

[0048]

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

[0049]



[0050]

Catalyst

5 In the elimination reaction step of the present disclosure, the elimination reaction is preferably performed in the presence of a catalyst in a gas phase.

[0051]

The catalyst for use in this step is preferably
 10 activated carbon. The catalyst for use in this step is preferably a metal catalyst. The metal catalyst is preferably at least one member selected from the group consisting of chromium oxide, fluorinated chromium oxide, chromium fluoride, aluminum oxide, fluorinated aluminum oxide, aluminum fluoride, iron oxide,
 15 fluorinated iron oxide, iron fluoride, nickel oxide, fluorinated nickel oxide, nickel fluoride, magnesium oxide, fluorinated magnesium oxide, and magnesium fluoride.

[0052]

Of these catalysts, activated carbon, chromium oxide,
 20 fluorinated chromium oxide, aluminum oxide, and fluorinated aluminum oxide are more preferable from the standpoint of obtaining the target compound at a higher selectivity. These catalysts can also increase the conversion rate of the starting material compound.

25 [0053]

In this step, when bringing the starting material compound into contact with a catalyst in a gas phase, it is preferable to bring the starting material compound into contact with the catalyst in a solid form (solid phase).

30 [0054]

In this step, the catalyst may be in the form of a

powder. However, the form of a pellet is preferable for the reaction in gas-phase continuous flow mode.

[0055]

The specific surface area ("BET specific surface area" below) of the catalyst according to BET theory is typically 10 to 3,000 m²/g, preferably 10 to 400 m²/g, more preferably 20 to 375 m²/g, and still more preferably 30 to 350 m²/g. A catalyst with a BET specific surface area within these numerical ranges does not have an overly low particle density, thus making it possible to obtain the target compound at a high selectivity. Such a catalyst can also increase the conversion rate of the starting material compound.

[0056]

Activated carbon for use as a catalyst is preferably powdered activated carbon of crushed charcoal, briquette, granular charcoal, spherical charcoal, or the like. The powdered activated carbon for use is preferably one that has a particle size of 4 mesh (4.76 mm) to 100 mesh (0.149 mm) in a JIS test.

[0057]

The metal catalyst for use is preferably supported on a carrier. Examples of carriers include carbon, alumina (Al₂O₃), zirconia (ZrO₂), silica (SiO₂), and titania (TiO₂). The carbon for use includes activated carbon, amorphous carbon, graphite, and diamond.

[0058]

The following explains chromium oxide and fluorinated chromium oxide as an embodiment of the catalyst of the present disclosure. For example, when chromium oxide is represented by Cr₂O₃·nH₂O, n is preferably 3 or less, and more preferably 1 to 1.5. When chromium oxide is represented by formula: CrO_m, m is preferably within the range of 1.5 < m < 3.

Fluorinated chromium oxide as a catalyst can be prepared by fluorinating chromium oxide. Fluorination includes fluorination by using hydrogen fluoride (HF) and fluorination by using a fluorocarbon or the like.

[0059]

Fluorinated chromium oxide as a catalyst can be obtained, for example, in accordance with the method disclosed in Japanese Patent No. 3412165. Fluorinated chromium oxide can be
5 obtained by subjecting chromium oxide to fluorination (HF treatment) by using hydrogen fluoride. The temperature of fluorination is, for example, preferably 100 to 460°C. The pressure of fluorination is preferably the pressure under a catalyst reaction. In the present disclosure, a highly
10 fluorinated chromium oxide catalyst with a high fluorine content is particularly preferable for use. The highly fluorinated chromium oxide catalyst can be obtained by fluorinating chromium oxide at a temperature higher than usual for a long time.

[0060]

15 The highly fluorinated chromium oxide catalyst preferably contains fluorine in an amount of 30 mass% or more, and more preferably 30 to 45 mass%. The amount of fluorine can be determined from the change in mass of the catalyst, or measured by typical quantitative analysis of chromium oxide.

20 [0061]

Elimination Reaction Temperature

In the elimination reaction step of the present disclosure, the lower limit of the reaction temperature is typically 50°C, preferably 200°C, more preferably 250°C, still
25 more preferably 300°C, and particularly preferably 350°C from the standpoint of more efficiently performing the elimination reaction to obtain the target compound at a higher selectivity and suppressing a decrease in conversion rate.

[0062]

30 The upper limit of the reaction temperature in the elimination reaction is typically 500°C, preferably 450°C, and more preferably 400°C from the standpoint of more efficiently performing the dehydrofluorination reaction to obtain the target compound at a higher selectivity and suppressing a decrease in
35 selectivity due to decomposition or polymerization of the

reaction product.

[0063]

Elimination Reaction Time

Regarding the time period of the elimination reaction,
5 as the contact time (W/F_0) [W : weight of metal catalyst (g), F_0 :
flow rate of starting material compound (cc/sec)] between the
starting material compound and the catalyst increases, the
conversion rate of the starting material compound increases.
However, due to the need for a larger amount of the catalyst, a
10 longer reaction time requires larger equipment, and is thus
inefficient.

[0064]

Thus, regarding the time period for the
dehydrofluorination reaction, the contact time (W/F_0) between the
15 starting material compound and the catalyst is preferably 5
 $\text{g}\cdot\text{sec}/\text{cc}$ to 300 $\text{g}\cdot\text{sec}/\text{cc}$, more preferably 10 $\text{g}\cdot\text{sec}/\text{cc}$ to 200
 $\text{g}\cdot\text{sec}/\text{cc}$, still more preferably 15 $\text{g}\cdot\text{sec}/\text{cc}$ to 150 $\text{g}\cdot\text{sec}/\text{cc}$, and
particularly preferably 20 $\text{g}\cdot\text{sec}/\text{cc}$ to 100 $\text{g}\cdot\text{sec}/\text{cc}$ from the
standpoint of increasing the conversion rate of the starting
20 material compound and reducing equipment costs.

[0065]

The contact time between the starting material compound
and the catalyst refers to the time period during which the
starting material compound and the catalyst are in contact with
25 each other.

[0066]

The target compound can be obtained at a higher
selectivity by adjusting the reaction temperature and the
reaction time (contact time), particularly so as to be suitable
30 for a catalyst in the elimination reaction of the present
disclosure performed in the presence of the catalyst in a gas
phase.

[0067]

When chromium oxide is used as a catalyst, the reaction
35 temperature is preferably 300°C or more, and more preferably

350°C or more. The contact time is preferably 10 g·sec/cc or more, more preferably 20 g·sec/cc or more, and still more preferably 40 g·sec/cc or more.

[0068]

5 When alumina is used as a catalyst, the reaction temperature is preferably 300°C or more, and the contact time is preferably 5 g·sec/cc or more.

[0069]

10 When activated carbon is used as a catalyst, the reaction temperature is preferably 300°C or more, more preferably 350°C or more, and still more preferably 400°C or more. The contact time is preferably 5 g·sec/cc to 55 g·sec/cc, more preferably 5 g·sec/cc to 50 g·sec/cc, and still more preferably 5 g·sec/cc to 40 g·sec/cc.

15 [0070]

Pressure in Elimination Reaction

20 The reaction pressure in the elimination reaction is preferably -0.05 MPa to 2 MPa, more preferably -0.01 MPa to 1 MPa, and still more preferably ordinary pressure to 0.5 MPa from the standpoint of more efficiently performing the elimination reaction. In present disclosure, the pressure is a gauge pressure unless indicated otherwise.

[0071]

25 In the elimination reaction, the reactor in which a starting material compound and a catalyst (e.g., a metal catalyst) are brought into contact with each other and reacted is not limited in terms of shape and structure as long as the reactor is resistant to temperature and pressure. Examples of reactors include vertical reactors, horizontal reactors, and 30 multi-tube reactors. Examples of reactor materials include glass, stainless steel, iron, nickel, and iron nickel alloy.

[0072]

Examples of Elimination Reaction

35 The elimination reaction can be performed in flow mode in which a starting material compound is continuously added to a

reactor, and a target compound is continuously taken out from the reactor, or the elimination reaction can be performed in batch mode. Because a target compound remaining in the reactor allows the elimination reaction to further proceed, the elimination
5 reaction is preferably performed in flow mode. In the elimination reaction step of the present disclosure, the elimination reaction is performed in a gas phase, particularly preferably in gas-phase continuous flow mode by using a fixed-bed reactor. The elimination reaction performed in gas-phase continuous flow mode
10 can simplify the equipment, operation, etc., and is also economically advantageous.

[0073]

The atmosphere in which the elimination reaction is performed is preferably an atmosphere in which inert gas and/or
15 hydrogen fluoride is present from the standpoint of suppressing the degradation of the catalyst (e.g., a metal catalyst). The inert gas is preferably at least one member selected from the group consisting of nitrogen, helium, argon, and carbon dioxide. Of these inert gasses, nitrogen is more preferable from the
20 standpoint of reducing costs. The concentration of the inert gas is preferably 0 to 50 mol% of the gas component introduced into the reactor.

[0074]

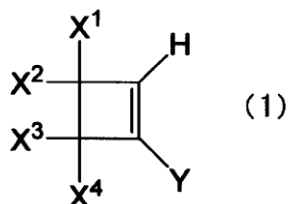
After completion of the elimination reaction, a
25 purification treatment can be optionally performed in accordance with an ordinary method to obtain the halogen atom-containing cyclobutene represented by formula (1).

[0075]

(3) Target Compound

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

[0076]



[0077]

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

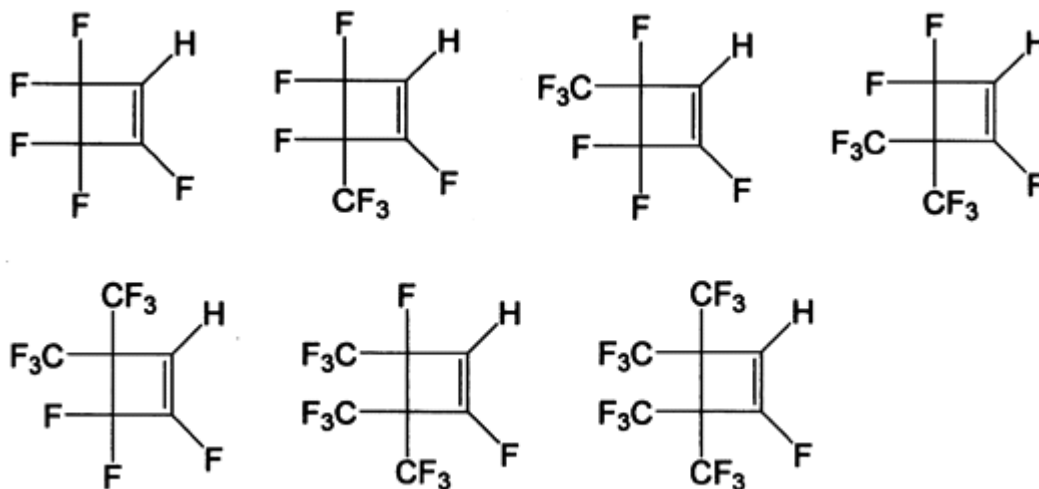
[0078]

X¹, X², X³, X⁴, and Y are as defined above.

[0079]

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

[0080]



[0081]

15 [0082]

The halogen atom-containing cyclobutene represented by
 formula (1) is preferably a cyclobutene 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 is a fluorine
 20 atom. The halogen atom-containing cyclobutene represented by
 formula (1) is more preferably a cyclobutene wherein X¹, X², X³,
 and X⁴ are a fluorine atom, and Y is a fluorine atom.

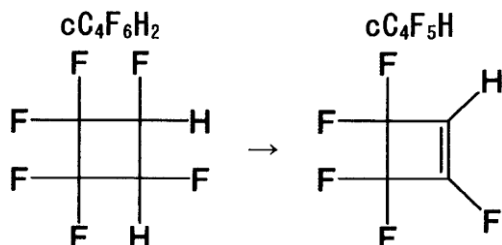
[0083]

In the method for producing a halogen atom-containing cyclobutene according to present disclosure, the starting material compound for the elimination reaction is preferably a
5 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.

[0084]

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

[0085]



15 [0086]

The target compound is preferably 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.

[0087]

20 (4) Composition Containing Halogen Atom-Containing Cyclobutene

In the manner described above, a halogen atom-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
25 the form of a composition containing a halogen atom-containing cyclobutene represented by formula (1) and a halogen atom-containing cyclobutane represented by formula (2).

[0088]

30 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

is a fluorine atom.

[0089]

In the composition containing the halogen atom-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 95 mol% or more, and more preferably 99 mol% or more based on the total amount of the composition taken as 100 mol%.

[0090]

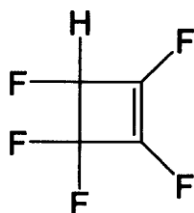
In the composition containing the halogen atom-containing cyclobutene represented by formula (1) according to present disclosure, the halogen atom-containing cyclobutene represented by formula (1) is preferably present in an amount of 1 mol% to 99.9 mol%, more preferably 5 mol% to 99.9 mol%, and still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

[0091]

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.

[0092]

cC₄F₅H (3H-cC₄F₅H)



[0093]

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%.

[0094]

The production method according to present disclosure produces the halogen atom-containing cyclobutene represented by
5 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 the cyclobutene. Thus, it is possible to reduce the components other than the halogen atom-containing cyclobutene represented by formula (1) in
10 the composition. The production method according to the present disclosure can reduce the labor for purification to obtain the halogen atom-containing cyclobutene represented by formula (1).

[0095]

The composition containing the halogen atom-containing
15 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
20 the same manner as with the halogen atom-containing cyclobutene represented by formula (1) alone.

[0096]

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

25 [0097]

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
30 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 CF_3 group, and this converts the cyclobutene or the composition into a substance that can be used as a cleaner or a
35 fluorine-containing pharmaceutical intermediate.

[0098]

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

Examples

[0099]

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

[0100]

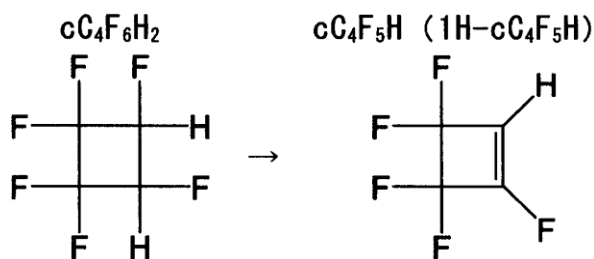
Example

In the Examples, the method for producing a halogen
15 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.

[0101]

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

[0102]



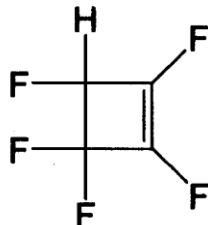
25 [0103]

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.

[0104]

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

[0105]



[0106]

5 Examples 1 to 3: Chromium Oxide Catalyst

10 10 g of chromium oxide that contains Cr_2O_3 as the major component (catalyst) was placed in an SUS pipe (outer diameter: 1/2 inch; reaction tube). The catalyst was subjected to a fluorination treatment as a pretreatment before use in the elimination reaction (dehydrofluorination) by circulating anhydrous hydrogen fluoride in the reactor and setting the reactor temperature to 200°C to 300°C . The fluorinated chromium oxide was taken out and used in a dehydrofluorination reaction. The fluorinated chromium oxide had a BET specific surface area of 15 $75 \text{ m}^2/\text{g}$.

[0107]

20 10 g of the fluorinated chromium oxide (catalyst) was placed in an SUS pipe (outer diameter: 1/2 inch, reactor). In a nitrogen atmosphere, the fluorinated chromium oxide was dried at 200°C for 2 hours, and a starting material compound ($\text{cC}_4\text{F}_6\text{H}_2$) was circulated in the reactor such that the pressure was ordinary pressure, and the contact time (W/F_0) between $\text{cC}_4\text{F}_6\text{H}_2$ (starting material compound) and the fluorinated chromium oxide (catalyst) was $20 \text{ g}\cdot\text{sec}/\text{cc}$ or $40 \text{ g}\cdot\text{sec}/\text{cc}$.

25 [0108]

The reaction was performed in gas-phase continuous flow mode.

[0109]

30 After the reactor was heated at 250°C or 350°C , a dehydrofluorination reaction was started.

[0110]

After one hour from the start of the dehydrofluorination reaction, the distillate that passed through the abatement tower was collected.

5 [0111]

After that, 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).

[0112]

The results of the mass spectrometry and structural analysis indicated that $\text{cC}_4\text{F}_5\text{H}$ was formed as a target compound. In Example 1, the conversion rate from $\text{cC}_4\text{F}_6\text{H}_2$ (starting material compound) was 3.34 mol%, and the selectivity (yield) for $\text{cC}_4\text{F}_5\text{H}$ (target compound) was 45.9 mol%. In Example 2, the conversion rate was 29.1 mol%, and the selectivity was 98.6 mol%. In Example 3, the conversion rate was 26.1 mol%, and the selectivity was 97.2 mol%.

[0113]

Examples 4 and 5: Alumina Catalyst

In accordance with the experiment in Example 1, alumina that contains Al_2O_3 as the major component was used as a catalyst. In accordance with the experiment in Example 1, a starting material compound ($\text{cC}_4\text{F}_6\text{H}_2$) was circulated in the reactor such that the contact time (W/F_0) between $\text{cC}_4\text{F}_6\text{H}_2$ (starting material compound) and alumina (catalyst) was 10 g·sec/cc or 40 g·sec/cc. In accordance with the experiment in Example 1, the reactor was heated at 400°C, and then a dehydrofluorination reaction was started. In the same manner as in Example 1, except for the conditions above, dehydrofluorination, mass spectrometry, and structural analysis were performed.

[0114]

35 The results of mass spectrometry and structural

analysis indicate that $\text{C}_4\text{F}_5\text{H}$ was formed as a target compound. In Example 4, the conversion rate from $\text{C}_4\text{F}_6\text{H}_2$ (starting material compound) was 7.92 mol%, and the selectivity for $\text{C}_4\text{F}_5\text{H}$ (target compound) was 45.1 mol%. In Example 5, the conversion rate was 4.11 mol%, and the selectivity was 35.0 mol%.

[0115]

Examples 6 to 10: Activated Carbon Catalyst

In accordance with the experiment of Example 1, activated carbon was used as a catalyst. In accordance with the experiment in Example 1, a starting material compound was circulated in the reactor such that the contact time (W/F_0) between $\text{C}_4\text{F}_6\text{H}_2$ (starting material compound) and activated carbon (catalyst) was 10 g·sec/cc, 27 g·sec/cc, or 47 g·sec/cc. In accordance with the experiment in Example 1, the reactor was heated at 300°C, 350°C, or 400°C, and then a dehydrofluorination reaction was started. In the same manner as in Example 1, except for the conditions above, dehydrofluorination, mass spectrometry, and structural analysis were performed.

[0116]

The results of mass spectrometry and structural analysis indicate that $\text{C}_4\text{F}_5\text{H}$ was formed as the target compound. In Example 6, the conversion rate from $\text{C}_4\text{F}_6\text{H}_2$ (starting material compound) was 57.6 mol%, and the selectivity for $\text{C}_4\text{F}_5\text{H}$ (target compound) was 95.3 mol%. In Example 7, the conversion rate was 97.7 mol%, and the selectivity was 68.3 mol%. In Example 8, the conversion rate was 84.1 mol%, and the selectivity was 83.8 mol%. In Example 9, the conversion rate was 72.3 mol%, and the selectivity was 94.6 mol%. In Example 10, the conversion rate was 84.7 mol%, and the selectivity was 95.7 mol%.

[0117]

Table 1 below illustrates the results of the Examples. In Table 1, the contact time (W/F_0) refers to the rate at which the starting material gas is circulated, i.e., the time period during which the catalyst and the starting material gas are in contact with each other.

[0118]

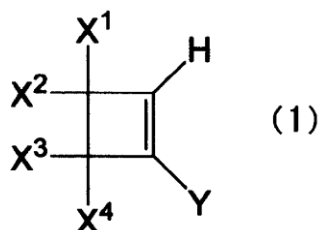
Table 1

Examples	Type of Catalyst	Reaction Temperature (°C)	Contact Time W/F ₀ (gsec/cc)	Conversion Rate from Starting Material cC ₄ F ₆ H ₂ (mol%)	Selectivity for Target Compound 1H-cC ₄ F ₅ H (mol%)	Selectivity for 3H-cC ₄ F ₅ H (mol%)	Other Generated Products (mol%)
1	Chromium Oxide	250	40	3.34	45.9	0.02	54.08
2	Chromium Oxide	350	40	29.1	98.6	0.05	1.39
3	Chromium Oxide	350	20	26.1	97.2	0.06	2.75
4	Alumina	400	40	7.92	45.1	0.02	54.8
5	Alumina	400	10	4.11	35.0	0.02	65.0
6	Activated Carbon	400	10	57.6	95.3	0.07	4.6
7	Activated Carbon	400	47	97.7	68.3	0.11	31.6
8	Activated Carbon	400	27	84.1	83.8	0.18	16.0
9	Activated Carbon	300	47	72.3	94.6	0.11	5.3
10	Activated Carbon	350	47	84.7	95.7	0.15	4.1

CLAIMS

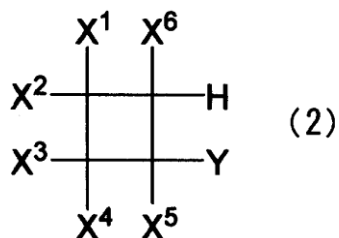
[Claim 1]

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



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

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



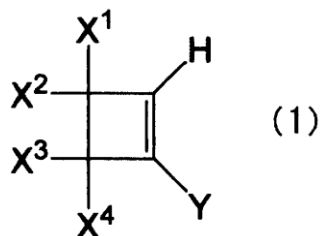
15 wherein X¹, X², X³, X⁴, and Y are as defined above, and X⁵ and X⁶ are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group,
20 wherein the elimination reaction is performed in a gas phase.

[Claim 2]

The method according to claim 1, wherein X⁵ represents a hydrogen atom, X⁶ represents a halogen atom, and the elimination
25 reaction is a dehydrohalogenation reaction.

[Claim 3]

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



5 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, wherein the cyclobutene represented by formula (1) is present in an amount of 95 mol% or more based on the total amount of the
10 composition taken as 100 mol%.

[Claim 4]

 The composition according to claim 3, wherein 1H-perfluorocyclobutene (1H- $\text{C}_4\text{F}_5\text{H}$) is present in an amount of 99
15 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.

[Claim 5]

 The composition according to claim 3 or 4, which is for
20 use in cleaning gas, etching gas, deposit gas, or a building block for organic synthesis.