PROCESS FOR PRODUCING FLUORINE-CONTAINING PROPENE COMPOUND

The present invention provides a process for producing a fluorine-containing propene compound represented by Formula (2): CF₂FCH=CH₂ wherein X is F, Cl, or H, the process including reducing a compound represented by Formula (1): CF₂XCF=CCl₂ wherein X is the same as the above, with hydrogen in the presence of a catalyst. The process according to the present invention is suitable for industrial production, and ensures simple and efficient production of the fluorine-containing propene compound represented by Formula (2): CF₂XCF=CH₂ wherein X is F, Cl, or H.
Title of Invention: PROCESS FOR PRODUCING FLUORINE-CONTAINING PROPENE COMPOUND

Technical Field
The present invention relates to a process for producing fluorine-containing propene compounds, such as compounds represented by CF₃CF=CH₂ (HFC-1234yf), compounds represented by CF₂ClCF=CH₂ (HCFC-1233yf), and the like.

Background Art
2,3,3,3-tetrafluoropropene represented by the formula: CF₃CF=CH₂ (HFC-1234yf) is useful as a refrigerant, and has attracted attention as a constituent of a refrigerant or a mixed refrigerant available as an alternative to chlorofluorocarbon. Further, a compound represented by the formula: CF₂ClCF=CH₂ (HCFC-1233yf) is a useful intermediate for the production of various fluorocarbons.

As one example of processes for producing HFC-1234yf among these compounds, Non-Patent Literature (NPL) 1 discloses a process comprising only one step: reacting a compound represented by CF₃CF₂CHₓ X = Cl or I) with zinc in ethanol. However, this process is not suitable for industrial production because of the high cost of zinc and large amounts of waste. Patent Literature (PTL) 1 also describes that a mixture including at least 50% of HFC-1234yf is obtained by carrying out HF-elimination of CF₃CF₂CHCl₂ (HCFC-225ca) to synthesize CF₃CF=CCl₂ (HFC-1214ya), and then reducing HFC-1214ya with hydrogen in a gas phase in the presence of a palladium catalyst supported on alumina, fluorinated alumina, aluminum fluoride or a mixture thereof. This process, however, does not provide a satisfactory yield, and further improvement is desired.

In addition, HFC-1234yf is reportedly produced by a reaction of chloromethyl tetrafluoropropanoate with amine (PTL 2); by thermal decomposition of 1-trifloromethyl-1,2,2-
trifluorocyclobutane (PTL 3), by a reaction of chlorotrifluoroethylene (CClF=CF₂) with methyl fluoride (CH₃F) in the presence of a Lewis acid represented by SbF₅ (PTL 4); or by thermal decomposition of tetrafluoroethylene (CF₂=CF₂) and chloromethane (CH₃Cl) (PTL 5). Additionally, NPL 2 and NPL 3 disclose processes for producing HFC-1234yf.

However, these processes are not sufficiently effective for industrial production due to a difficulty in the production and procurement of the starting materials, severe reaction conditions, high costs for the reaction reagent, a low yield, or other drawbacks.

On the other hand, as one example of processes for producing CF₂ClCF=CH₂ (HCFC-1233yf), PTL 6 discloses a process for carrying out HCl-elimination of CF₂CICFCICH₃ (HCFC-243bc); however, the starting materials for this process are extremely difficult to obtain.

Citation List
Patent Literature
PTL 1: WO 2008/060614 A2
PTL 3: U.S. Patent No. 3996299
PTL 5: U.S. Patent No. 2931840
PTL 6: U.S. Patent No. 2996555
Non Patent Literature

Summary of Invention
Technical Problem

The present invention has been accomplished in view of the problems of the prior art described above. A main object of the present invention is to provide a simple and efficient
process for producing a fluorine-containing propene compound represented by Formula (2) : \( \text{CF}_2\text{XCF}=\text{CH}_2 \) wherein \( \text{X} \) is \( \text{F}, \text{Cl}, \text{or H} \), that is suitable for industrial production.

5 Solution to Problem

The present inventors conducted extensive research to achieve this object. As a result, the inventors found that a fluorine-containing propene compound represented by Formula (2) : \( \text{CF}_2\text{XCF}=\text{CH}_2 \) wherein \( \text{X} \) is \( \text{F}, \text{Cl}, \text{or H} \), can be simply and efficiently produced in a high yield by reducing a halogenated propene compound represented by Formula (1) : \( \text{CF}_2\text{XCF}=\text{CCl}_2 \) wherein \( \text{X} \) is the same as the above, with hydrogen in the presence of a catalyst. The present invention has been accomplished on the basis of this finding.

More specifically, the present invention provides the following process for producing a fluorine-containing propene compound:

Item 1. A process for producing a fluorine-containing propene compound represented by Formula (2) : \( \text{CF}_2\text{XCF}=\text{CH}_2 \) wherein \( \text{X} \) is \( \text{F}, \text{Cl}, \text{or H} \), the process comprising reducing a compound represented by Formula (1) : \( \text{CF}_2\text{XCF}=\text{CCl}_2 \) wherein \( \text{X} \) is the same as the above, with hydrogen in the presence of a catalyst.

Item 2. The process according to Item 1, wherein the catalyst is a palladium-carbon catalyst.

Item 3. The process according to Item 2, wherein the palladium-carbon catalyst is poisoned with sulfur using 0.1 to 5 mol of poisoning agent per mol of the palladium in the catalyst.

Item 4. The process according to any one of Items 1 to 3, wherein the reduction reaction is carried out in the presence of a base, in water as a reaction medium.

Item 5. The process according to any one of Items 1 to 4, wherein the reaction temperature is -5 to 50°C.

In the process according to the present invention, a halogenated propene compound represented by Formula (1) :
CF₂XCF=CCl₂ wherein X is F, Cl, or H, is used as a starting material. For example, a compound represented by the formula: CF₃CF=CCl₂ (CFC-1214ya), a compound represented by the formula: CF₂ClCF=CCl₂ (CFC-1213ya), and the like can be used. Such starting compounds can be produced by known methods. For example, they can be easily obtained by an HF-elimination reaction of a compound represented by Formula (3): CF₂XCF₂CHCl₂ wherein X is F, Cl, or H. Among the above compounds represented by Formula (1), the compound represented by CF₃CF=CCl₂ (CFC-1214ya) is produced from a compound represented by CF₃CF₂CHCl₂ (HCFC-225ca), and the compound represented by the formula: CF₂ClCF=CCl₂ (CFC-1213ya) is produced from a compound represented by the formula: CF₂ICF₂CHCl₂ (HCFC-224ca). Using these compounds, HF-elimination can be performed with KOH in the presence of a phase-transfer catalyst (e.g., Aliquat 336 \( \text{N}^+\text{(CH₃)}(\text{n-OC})₃\text{-Cl}^- \)) to synthesize the starting compounds of the present invention. Alternatively, the starting compounds can be produced by or based on the method described in the Bulletin de l'Association Société Chimique de France, (6), pp. 920-4, 1986.

According to the process of the present invention, the target fluorine-containing propene compound represented by Formula (2): CF₂XCF=CH₂ wherein X is F, Cl, or H, can be obtained by using the above-mentioned halogenated propene compound represented by Formula (1): CF₂XCF=CCl₂ wherein X is F, Cl, or H, as a starting material, and reducing the compound with hydrogen in the presence of a catalyst.

A preferable catalyst for the hydrogen reduction reaction is, although not limited to, palladium. It is preferable to use a palladium catalyst as a palladium-carbon (Pd-C) catalyst in which palladium is supported on activated carbon. The amount of the palladium is preferably 0.001 to 0.2 parts by weights, and more preferably about 0.005 to 0.1 parts by weight, per part by weight of the support.

In the present invention, it is particularly preferable to poison the catalyst with sulfur before use. The use of such a
sulfur-poisoned catalyst moderately reduces the activity of the catalyst to inhibit the addition reaction of hydrogen to a double bond, enhancing the selectivity of the target compound.

For example, the palladium catalyst can be poisoned by adding potassium sulfate (K₂SO₄), barium sulfate (BaSO₄), sodium sulfate (Na₂SO₄), or other sulfur-containing compounds as a poisoning agent to an aqueous suspension of the palladium catalyst, followed by sufficient mixing. The amount of the poisoning agent is preferably about 0.1 to 5 mol, and more preferably about 1 to 3 mol, per mol of the palladium in the catalyst. The time required for the poisoning treatment is not limited, but is, for example, set about 5 to 60 minutes.

The poisoning treatment of the palladium catalyst can be performed in a reactor before introducing hydrogen for the hydrogenation reaction. For example, the poisoning treatment may be carried out by adding a palladium catalyst and a poisoning agent to water, which is used as a reaction medium, before adding a starting material; thereafter, the starting material, i.e. halogenated propene compound represented by Formula (1): CF₂XCF=CCl₂, is added to the water in which the poisoned palladium catalyst is dispersed; and hydrogen is introduced to perform a hydrogenation reaction. Alternatively, the poisoning treatment may be carried out by adding halogenated propene compound, which is the starting material, to water (reaction medium) together with a palladium catalyst and a poisoning agent, and sufficiently stirring the mixture; and then hydrogen is introduced to perform a hydrogenation reaction.

When using a palladium-carbon (Pd-C) catalyst in the present invention, the amount of the catalyst is preferably about 0.001 to 0.01 parts by weight, and more preferably about 0.002 to 0.008 parts by weight, per part by weight of the compound represented by Formula (1).

In the present invention, water can generally be used as a reaction medium for the hydrogen reduction reaction of the compound of Formula (1). More specifically, the halogenated
propene compound represented by Formula (1) and a catalyst may be mixed and uniformly suspended in water, which is used as a reaction medium, and the suspension may be brought into contact with hydrogen.

Generally, the amount of water used as a reaction medium is preferably about 1 to 10 parts by weight, and more preferably about 3 to 7 parts by weight, per part by weight of the compound represented by Formula (1). In addition to water, ethanol, methanol, propanol, and other hydrophilic solvents may be added as reaction mediums in an amount of about 0.1 to 5 parts by weight, per part by weight of the water.

According to the process of the present invention, a base is added to water containing the halogenated propene compound represented by Formula (1) and a catalyst in order to neutralize HCl generated by the reaction. Any bases can be used as long as they can neutralize HCl. Preferable examples include KOH, NaOH, CH<sub>3</sub>CO<sub>2</sub>Na, etc. The amount of the base used is preferably about 2 to 2.4 mol, and more preferably about 2 to 2.2 mol, per mol of the compound represented by Formula (1).

The process of the present invention can usually be carried out in batch mode. For example, the hydrogenation reaction of the halogenated propene compound represented by Formula (1) can be performed in such a manner that the halogenated propene compound of Formula (1), a base, and a catalyst are uniformly dispersed in water; the mixture is put in a reactor; hydrogen is introduced into the reactor; and the mixture is stirred.

The amount of hydrogen used is preferably about 2 to 2.4 mol, and more preferably about 2.1 to 2.3 mol, per mol of the halogenated propene compound represented by Formula (1). Although the pressure in the reactor is not limited, usually the partial pressure of hydrogen is preferably about 0.05 to 1.0 MPa-G, and more preferably about 0.1 to 0.8 MPa-G.

Generally, the reaction temperature is preferably about -5 to 50°C, and more preferably about 0 to 20°C. Temperatures
outside this range are not preferable. At reaction temperatures below -50°C, an aqueous solution cannot be stirred because the solution is solidified. On the other hand, at temperatures above 50°C, the reduction reaction excessively proceeds, raising the production of by-products.

Although the reaction time varies depending on the reaction conditions, it is usually about 12 to 48 hours. The progress of the reaction can be monitored by taking a gas sample from the reaction system and analyzing the components of the gas phase using gas chromatography. The obtained 2,3,3,3-tetrafluoropropene (HFC-1234yf) and CF₂ClCF=CH₂ (HCFC-1233yf) have boiling points as low as -28.3°C and 11.9°C, respectively; therefore, the resultant products of the reaction can be collected by fractional distillation or a like method, using a freezing mixture.

Using such a process, the fluorine-containing propene compound represented by Formula (2): CF₂XCF=CH₂ can be produced from the compound represented by Formula (1): CF₂XCF=CCl₂, while ensuring a high conversion, selectivity, and isolated yield.

The fluorine-containing propene compound of Formula (2) obtained by the process of the present invention can be used in various applications. For example, 2,3,3,3-tetrafluoropropene (HFC-1234yf), which has a low warming potential and a low ozone depletion potential, is useful as, for example, a constituent for a mixed refrigerant that functions as an alternative to chlorofluorocarbon. Moreover, the compound represented by CF₂ClCF=CH₂ (HCFC-1233yf) is useful as an intermediate for the production of various fluorocarbons.

Advantageous Effects of Invention

The process according to the present invention ensures simple and efficient production of 2,3,3,3-tetrafluoropropene (HFC-1234yf), CF₂ClCF=CH₂ (HCFC-1233yf), and like compounds represented by the formula: CF₂XCF=CH₂.

The process has some advantages including the use of an
inexpensive reagent, moderate reaction conditions, and a high yield of target compounds. These advantages make the process of the present invention suitable for industrial production.

Description of Embodiments

Examples are provided below to clarify features of the present invention. The present invention, however, is not limited to these examples.

Example 1

Pd-C catalyst (0.0681 g; type-K; produced by NE-Chemcat; 5 wt% Pd, carbon of 50% moisture content), 0.0112 g of K₂SO₄, and 100 ml (104 g) of 1 N potassium hydroxide solution were placed in a 200-ml SUS autoclave (reactor) equipped with a pressure gauge, a thermometer, a gas removal valve, and a safety valve. After adding 9.8 g (0.0536 mol) of CF₃CF=CCl₂ (CFC-1214ya, purity: 99.3%), the mixture was sufficiently suspended using a mechanical stirrer.

Under ice-cooling, the reactor was purged with nitrogen, followed by pressure reduction using a vacuum pump. Then, a hydrogen cylinder (filled with hydrogen gas (47 L, 14.7 MPa)) was connected to the reactor.

After the above-mentioned process was completed, the reaction mixture was stirred at 500 rpm, and held at 1 to 2°C using ice water. The pressure at this time was -0.02 MPa-G. Under these conditions, hydrogen was supplied from the hydrogen cylinder connected to the reactor until the internal pressure of the autoclave became 0.8 MPa-G. After 5 hours, the internal pressure decreased to around 0.2 MPa-G and hydrogen was again supplied in the same manner. This process was repeated for 17 hours until a total of 0.1185 mol (2653 cc) of hydrogen was supplied. While keeping the temperature of the reaction mixture at 1 to 8°C during the reaction, a gas sample was taken at times, and the composition of the gas phase was analyzed using gas chromatography. The reaction was carried out for a total of 21 hours. The internal pressure of the reactor at this time was 0.14
After the reaction was completed, the gas component was removed from the reactor at a temperature of 1 to 2°C. Subsequently, the reactor was heated to an internal temperature of 40°C, and all the organic compounds were taken out. Since the boiling point of the main product (HFC-1234yf) was -28.3°C, the product was collected using a freezing mixture made of dry ice and acetone. The collected product weighed 6.33 g. The collected product was analyzed using gas chromatography; the CFC-1214ya conversion was 97.9%, the HFC-1234yf selectivity was 75.6%, and the isolation yield was 74.0%. The by-products were CF₃CF=CHCl (HCFC-1224yd), CF₃CHFCH₃ (HFC-254eb), and CF₃CHFCH₂Cl (HCFC-244eb); and the selectivities were 4.9%, 17.5%, and 2.0%, respectively.

Example 2

Pd-C catalyst (0.0635 g; type-K; produced by NE-Chemcat; 5 wt% Pd, carbon of 50% moisture content), 0.0117 g of K₂SO₄, and 100 ml (104 g) of 1 N potassium hydroxide solution were placed in a 200-ml SUS autoclave (reactor) equipped with a pressure gauge, a thermometer, a gas removal valve, and a safety valve. After adding 10.1 g (0.0506 mol) of CF₂ClCF=CCl₂ (CFC-1213ya, purity: 99.3%), the mixture was sufficiently suspended using a mechanical stirrer.

Under ice-cooling, the reactor was purged with nitrogen, followed by pressure reduction using a vacuum pump. Then, a hydrogen cylinder (filled with hydrogen gas (47 L, 14.7 MPa)) was connected to the reactor.

After the above-mentioned process was completed, the reaction mixture was stirred at 500 rpm, and held at 1 to 2°C using ice water. The pressure at this time was -0.04 MPa-G. Under these conditions, hydrogen was supplied from the hydrogen cylinder connected to the reactor until the internal pressure of the autoclave became 0.8 MPa-G. After 6.5 hours, the internal pressure decreased to around 0.3 MPa-G and hydrogen was again supplied in the same manner. This process was repeated for 34
hours until a total of 0.1144 mol (2562 cc) of hydrogen was supplied. While keeping the temperature of the reaction mixture at 1 to 8°C during the reaction, a gas sample was taken at times, and the composition of the gas phase was analyzed using gas chromatography. The reaction was carried out for a total of 43 hours. The internal pressure of the reactor at this time was 0.19 MPa-G.

After the reaction was completed, the gas component was removed from the reactor at a temperature of 1 to 2°C. Subsequently, the reactor was heated to an internal temperature of 80°C, and all the organic compounds were taken out. The product was collected using a freezing mixture made of dry ice and acetone. The collected product weighed 6.67 g. The collected product was analyzed using gas chromatography; the CFC-1213ya conversion was 94.4%, the HCFC-1233yf selectivity was 67.3%, and the isolation yield was 63.5%. The by-products were CHF₂CF=CH₂ (HFC-1243yf), CHF₂CHFCH₃ (HFC-263eb), CF₂CICF=CHCl (HCFC-1223yd), and CF₂CICHFCH₂Cl (HCFC-243ec); the selectivities were 14.6%, 3.9%, 8.5%, and 2.8%, respectively; and the total selectivity of other by-products was 2.9%.
[Claim 1] A process for producing a fluorine-containing propene compound represented by Formula (2): CF₂XCF=CH₂ wherein X is F, Cl, or H, the process comprising reducing a compound represented by Formula (1): CF₂XCF=CCl₂ wherein X is the same as the above, with hydrogen in the presence of a catalyst.

[Claim 2] The process according to claim 1, wherein the catalyst is a palladium-carbon catalyst.

[Claim 3] The process according to claim 2, wherein the palladium-carbon catalyst is poisoned with sulfur using 0.1 to 5 mol of poisoning agent per mol of the palladium in the catalyst.

[Claim 4] The process according to any one of claims 1 to 3, wherein the reduction reaction is carried out in the presence of a base, in water as a reaction medium.

[Claim 5] The process according to any one of claims 1 to 4, wherein the reaction temperature is -5 to 50°C.
INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2009/062068

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C17/23

According to International Patent Classification (IPC) or to both national classification and IPC

B. RELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, BEILSTEIN Data, CHEMABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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D. Further documents are listed in the continuation of Box C

X See patent family annex

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20 August 2009

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