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(54) Title: METHOD FOR PRODUCING FLUORINATED ORGANIC COMPOUNDS

(57) Abstract: Disclosed are methods for producing fluorinated organic compounds, including hydrofluoropropenes, which preferably comprises converting at least one compound of formula (I): $\text{CF}_3\text{CHXCH}_2\text{X}$ (I) to at least one compound of formula (II) CF_3CZCHZ (II), where X is independently Cl, Br, I or F, and Z independently is H or F. In certain preferred embodiments, each Z is different.

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METHOD FOR PRODUCING FLUORINATED ORGANIC COMPOUNDS

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BACKGROUND OF INVENTION**(1) Field of Invention:**

This invention relates to novel methods for preparing fluorinated organic compounds, and more particularly to methods of producing fluorinated olefins.

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(2) Description of Related Art:

Hydrofluorocarbons (HFC's), in particular hydrofluoroalkenes such tetrafluoropropenes (including 2,3,3,3-tetrafluoro-1-propene (HFO-1234yf) and 1,3,3,3-tetrafluoro-1-propene (HFO-1234ze)) have been disclosed to be effective refrigerants, fire extinguishants, heat transfer media, propellants, foaming agents, blowing agents, gaseous dielectrics, sterilant carriers, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, displacement drying agents and power cycle working fluids. Unlike chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), both of which potentially damage the Earth's ozone layer, HFCs do not contain chlorine and thus pose no threat to the ozone layer.

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Several methods of preparing hydrofluoroalkanes are known. For example, U.S. Pat. No. 4,900,874 (Ihara et al) describes a method of making

fluorine containing olefins by contacting hydrogen gas with fluorinated alcohols. Although this appears to be a relatively high-yield process, for commercial scale production the handling of hydrogen gas at high temperature raises difficult safety related questions. Also, the cost of producing hydrogen gas, such as building an on-site hydrogen plant, can be in many situations prohibitive.

U.S. Pat. No. 2,931,840 (Marquis) describes a method of making fluorine containing olefins by pyrolysis of methyl chloride and tetrafluoroethylene or chlorodifluoromethane. This process is a relatively low yield process and a very large percentage of the organic starting material is converted in this process to unwanted and/or unimportant byproducts, including a sizeable amount of carbon black. The carbon black is not only unwanted, it tends to deactivate the catalyst used in the process.

The preparation of HFO-1234yf from trifluoroacetylacetone and sulfur tetrafluoride has been described. See Banks, et al., *Journal of Fluorine Chemistry*, Vol. 82, Iss. 2, p. 171-174 (1997). Also, U.S. Pat. No. 5,162,594 (Krespan) discloses a process wherein tetrafluoroethylene is reacted with another fluorinated ethylene in the liquid phase to produce a polyfluoroolefin product.

Notwithstanding prior teachings applicants appreciate a continuing need for methods of efficiently preparing certain hydrofluorocarbons, particularly tetrafluorpropenes such as HFO-1234yf and HFO-1234ze (including cis- and trans-forms thereof).

SUMMARY OF THE INVENTION

Applicants have developed a method for producing fluorinated organic compounds, including hydrofluoropropenes, which preferably comprises converting at least one compound of formula (I):



to at least one compound of formula (II)



where X is independently Cl or F, and Z independently is H or F. In certain preferred embodiments, each Z is different.

The preferred converting step of the present invention comprises dehydrohalogenating at least one compound of formula (I). The dehydrohalogenation step comprises in preferred embodiments introducing said at least one compound of formula (I) to a reaction system under conditions effective to convert, and preferably convert at least about 50%, and even more preferably at least about 70%, of said compound of formula (I). It is also generally preferred that said reaction step produces a reaction product having at least about 70% selectivity, and even more preferably at least about 80% selectivity, to compounds of formula (II). In certain highly preferred embodiments, the reaction step produces a reaction product having at least about 70% selectivity, and even more preferably at least about 80% selectivity, to, tetrafluoropropene, and even more preferably HFO-1234yf and/or HFO-1234ze.

In certain preferred embodiments, the converting step comprises reacting a compound of formula (I) in the gas phase, in the liquid phase, or a combination of these, with gas phase reactions preferably occurring in the presence of catalyst.

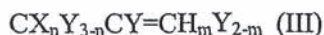
DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

One beneficial aspect of the present invention is that it enables the production of desirable fluoroolefins, preferably C3 fluoroolefins, from relatively attractive starting materials, and in preferred embodiments the present methods are capable of achieving very desirable levels of conversion of the starting materials while also providing high levels of selectivity to the desired products. Fluoropropenes in general, and trifluoropropenes in particular are in many embodiments an advantageous starting material because such products are relatively inexpensive, are relatively easy to handle, and are generally readily available in commercial quantities or can be easily produced from other readily available materials. For example trifluoropropene can be synthesized by the Cu-catalyzed liquid-phase coupling of CCl_4 and $\text{CH}_2=\text{CH}_2$, preferably followed by hydrofluorination.

Thus, in certain embodiments the present methods include the step of reacting fluorinated olefin, more preferably a fluorinated olefin having three carbon atoms, such as trifluoropropene, with a halogen addition agent, preferably a chlorine addition agent and/or a fluorine addition agent, under conditions effective to produce a compound of formula (I)



where X is independently Cl or F. In preferred embodiments, the fluorinated olefin reactant is a compound of formula (III)



where each X is independently Cl or F, each Y is independently H, Cl or F, n is 1, 2 or 3, and m is 1 or 2. In preferred embodiments, the compound of formula (III) comprises, and even more preferably consists essentially of $\text{CF}_3\text{CH}=\text{CH}_2$,

The reaction by which the compound of formula (III) is converted to a compound of formula (I) is sometimes referred to herein for convenience, but not necessarily by way of limitation, as a halogen addition reaction.

Preferably the formula (I) compound, which is preferably formed by a process comprising a halogen addition reaction, is then exposed to reaction conditions, which are sometimes referred to herein for convenience, but not necessarily by way of limitation, as a dehydrohalogenation reaction, to produce a reaction product containing one or more of the desired fluorolefins, preferably one or more compounds of formula (II). Preferred aspects of each of the preferred steps is described below, with the titles used as headings for these steps being used for convenience but not necessarily by way of limitation.

I. HALOGEN ADDITION

In preferred embodiments, the reactant compound of formula (III) is fluorinated olefin, more preferably fluorinated propylene and even more preferably $\text{CF}_3\text{CH}=\text{CH}_2$ (sometimes referred to herein as the “compound of formula (IIIA)”). It is further preferred that the halogen addition agent is a

compound of formula X_mY_{2-m} where X, Y and m are as described above.

Preferably, the halogen addition agent is one or more of ClF, Cl_2 , F_2 and HF.

For embodiments directed primarily to the production of $CF_3CF=CH_2$ (HFO-1234yf), it is generally preferred that the compound of formula (I) comprise
5 a compound of formula (IA)



that is, a compound in which X is F (HFC-245eb). In many preferred
embodiments, HFC-245eb is produced by a halogen addition reaction involving
trifluoropropene and a halogen addition agent comprising, and preferably
10 consisting essentially of, F_2 .

For embodiments directed primarily to the production of $CF_3CH=CHF$ (HFO-1234ze), it is generally preferred that the compound of formula (I)
comprise a compound of formula (IB)



15 In many preferred embodiments, the compound of formula (IB) is produced by a
halogen addition reaction involving trifluoropropene and a halogen addition agent
comprising, and preferably consisting essentially of, ClF.

In certain preferred embodiments, the halogen addition step comprises
contacting, (preferably by introducing into a reactor) the compounds in an
20 X_mY_{2-m} :formula (III) mole ratio of from about 0.01:1 to about 50:1, and even
more preferably of from about 0.1:1 to about 10:1. In preferred embodiments in
which the compound of X_mY_{2-m} comprises F_2 and the formula III compound
comprises $CF_3CH=CH_2$, the F_2 :trifluoropropene mole ratio of the feeds to the

reactor are from about 0.01:1 to about 10:1 and even more preferably from about 0.1:1 to about 1:1. In preferred embodiments in which the compound of X_mY_{2-m} comprises ClF and the formula III compound comprises $CF_3CH=CH_2$, the ClF:trifluoropropene mole ratio of the feeds to the reactor are from about 0.01:1 to about 10:1 and even more preferably from about 0.1:1 to about 2:1.

This reaction step can be carried out in the liquid phase or in the gas phase, and it is contemplated that the reaction can be carried out batch wise, continuous, or a combination of these.

A. PREFERRED LIQUID PHASE REACTIONS

Certain preferred embodiments of this reaction (particularly when the halogenation agent (the X_mY_{2-m} compound) is ClF, HF or Cl_2 , or combinations of two or more of these) involve relatively low temperature reactions in which at least the organic reactant(s) are charged to the reactor as liquids, with the reactor preferably maintained at least during a portion of the reaction at a temperature of from about $-90^\circ C$ to about $-18^\circ C$, and at least a portion of the reaction is carried in the liquid phase (the normal boiling point of the preferred reactant trifluoropropylene is $-18^\circ C$). However, it is contemplated that at least some portion of the reaction product may be produced and/or removed from the reaction mixture in such embodiments as a gaseous material. For example, it is preferred in certain embodiments to charge a reaction vessel, such as a stirred tank reactor, with the compound of formula (III), preferably formula (IIIA), so as to bring the contents of the reactor to a temperature of from about $-80^\circ C$ to about $-60^\circ C$, and

to then add ClF to the reaction vessel. Preferably the reaction mixture has kinetic energy added to provide a substantially uniform reaction mixture (such as stirring) for a time of from about 0.1 hour to about 1 hour at a temperature of from about -60°C to about -50°C. The temperature of the reaction mixture is then preferably raised to a temperature of about -20°C for a period of from about 0.5 hour to about 5 hour, preferably for about 3 hours, under vigorous stirring. The reaction mixture is then preferably cooled to a temperature of from about -60°C to about -40°C (preferably about -50°C) and water is added to the reactor at subzero temperature to neutralize the mineral acids such as HF and HCl formed during the reaction and reaction mixture is stirred for a period of from about 0.1 to about 0.5 hours. Water addition reaction is highly exothermic, thus, addition of water at around 0°C to -30°C is preferred to keep the exothermicity under control. The reactor temperature is then preferably raised to from about 10°C to about 30°C, preferably 20°C, and the gaseous products from the reactor are then preferably removed and transferred to a collection vessel.

For those preferred embodiments which utilize ClF as a reactant, it is sometimes preferred to provide source of chlorine and fluorine by the liquid-phase reaction of HF and Cl₂ in the presence of catalyst, preferably a transition metal catalyst, and even more preferably a transition metal halide catalysts such as FeCl₃, SnCl₄, TaCl₅, TiCl₄, SbCl₅, SbCl₃, and CrCl₃, SbF₃, SbF₅, AlF₃, and CrF₃, and combinations of two or more of these. In certain preferred embodiments, therefore, the present step comprises contacting CF₃CH=CH₂, HF and Cl₂ in the presence of a metal catalyst, preferably a metal chloride salt, preferably with

addition of kinetic energy to provide a substantially uniform reaction mixture (such as stirring), under conditions effective to form a reaction product comprising the desired compound of formula I. In certain preferred embodiments, the reaction is carried out, preferably at a temperature of from about -90°C to about -20°C, more preferably from about -50°C to about -30°C, under conditions effective to achieve a percentage conversion of at least about 30%, more preferably at least about 70%, and even more preferably at least about 100% of the compound of formula III. Preferably, the reaction conditions are effective to achieve a percentage selectivity to compounds of formula I, and preferably compounds of formula (IA) of at least about 30%, more preferably at least about 50% to at least about 75%, and even more preferably at least about 95%. In certain preferred embodiments a selectivity of about 98% or greater is achieved.

As used herein, the term "percentage conversion" with respect to a reactant, which typically is a limiting agent, refers to the moles reacted in the reaction process divided by the moles of that limiting reactant in the feed to the process multiplied by 100.

As used herein, the term "percentage selectivity" with respect to an organic reaction product refers to the ratio of the moles of that reaction product to the total of the organic reaction products multiplied by 100.

In certain preferred embodiments the reaction time for the preferred liquid phase reaction is from about 0.1 to about 3 hours. The reaction product in preferred embodiments in which ClF is the halogen addition agent includes one or more of $\text{CF}_3\text{CHClCH}_2\text{F}$, $\text{CF}_3\text{CHClCH}_2\text{Cl}$, $\text{CF}_3\text{CHFCH}_2\text{Cl}$, $\text{CF}_3\text{CH}_2\text{CH}_2\text{F}$ and/or

$\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$. In preferred embodiments, the reaction product comprises from about 40 wt. % to about 60 wt.% $\text{CF}_3\text{CHClCH}_2\text{F}$, from about 10 to about 30 wt. % $\text{CF}_3\text{CHClCH}_2\text{Cl}$, from about 5 to about 15 wt% $\text{CF}_3\text{CHFCH}_2\text{Cl}$, from about 5 to about 10 wt% $\text{CF}_3\text{CH}_2\text{CH}_2\text{F}$, and about 3 to about 8 wt% $\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$.

5 It will be appreciated that many alternatives for the provision of ClF in accordance with this preferred step of the present invention are available and within the scope hereof. By way of example, the reactant ClF may be provided in certain embodiments simply by purchasing the needed quantity of the material in the appropriate form. In other preferred embodiments, it is desirable to provide
10 the chlorine and fluorine conducting a liquid-phase reaction of HF and Cl_2 , preferably in the presence of transition metal halide such as SbF_5 , as described above or using similar reactions. Such reactions, especially single stage reactions, can be achieved using any equipment and conditions known and available in the art for such type of reaction, preferably at a temperature of from about -20°C to
15 about -90°C , and even more preferably the reaction temperature is maintained at a temperature of from about -20°C to about -50°C .

 As an alternative to the above mentioned single stage process, in certain embodiments a two stage scheme is used in which the reaction of HF and Cl_2 is carried out in a first vessel, stage or the like, and then in a second vessel, stage or
20 the like the compound of formula (III) is added to initiate the halogen addition reaction to form the compound of formula (I). In such embodiments, it is generally preferred that the first stage is a liquid phase reaction and the second

stage is also a liquid phase reaction. In such embodiments it is found that the conversion can be improved, preferably to at least about 80%.

B. PREFERRED GAS/LIQUID PHASE REACTIONS

5 The formation of a compound of formula I, particularly a compound of formula (IB) ($\text{CF}_3\text{CHFCH}_2\text{F}$) may also be carried out at least partially in a liquid phase reaction using F_2 as the halogen addition agent where the F_2 is introduced to the reaction mixture as a gas. For the purpose of convenience, but not by way of limitation, such a reaction arrangement is sometimes referred to herein as a
10 gas/liquid phase reaction. Thus, for certain preferred embodiments, particularly those preferred embodiments which utilize F_2 as a reactant, it is preferred to provide a compound of formula (I) by a reaction which is conducted primarily in the liquid phase but in which the F_2 reactant is introduced in the gas phase. In such embodiments HF is preferably used as a solvent (preferably an inert
15 solvent) for the reaction and a catalyst is not required. In certain of such preferred embodiments the F_2 is provided in diluted form, preferably blended with an inert gas, such as nitrogen, in amount of about 5 – 100% (preferably about 10%) of the total of F_2 and inert gas. The gas is preferably contacted with the compound of formula (III), preferably in some cases by bubbling the gas through the liquid in a
20 stirred tank reactor at a temperature of from about -20°C to about -55°C for a time of from about 0.5 to about 1.5 hours. Preferred reactor pressure is from about 15 to about 80 psia, and even more preferably from about 20 to about 70 psia. In such embodiments the conversion of the formula III compound, particularly

formula (IIIA) compounds, is preferably at least about 80 to about 100%, more preferably at least about 40 to about 60%, and selectivity to compounds of formula (I) is preferably at least about 30%, more preferably at least about 35%, and even more preferably at least about 40%.

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C. PREFERRED GAS PHASE REACTIONS

For certain preferred embodiments, particularly those preferred embodiments which utilize F_2 as a halogen addition agent, it is preferred to provide a compound of formula (I) by a gas-phase reaction. In such preferred
10 embodiments, the compound of formula (III) and the halogen addition agent are introduced into and appropriate reaction vessel in the form of a gas and the reactor is preferably maintained at a temperature of from about -18°C for a time of from about 5 minutes to about 16 hours, and the reaction products are produced mainly as liquids which separate from the gaseous reactants in the vessel. Preferred
15 reactor pressure is atmospheric. In such embodiments the conversion of the formula III compound, particularly formula (IIIA) compounds, is preferably at least about 5%, more preferably at least about 10%, and selectivity to compounds of formula (I) is preferably at least about 30%, more preferably at least about 35%, and even more preferably at least about 50%.

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II. FORMATION OF THE COMPOUND OF FORMULA II

The methods of the present invention preferably comprise contacting a compound of formula (I) with a dehydrohalogenation agent to produce a

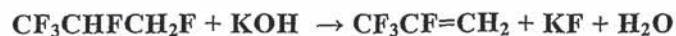
fluorolefin, preferably a C3 fluorolefin, more preferably a compound of formula (II), and even more preferably tetrafluoropropene.

In certain preferred embodiments, the present dehydrohalogenation step is carried out under conditions effective to provide a formula (I) conversion of at least about 40%, more preferably at least about 55%, and even more preferably at least about 70%. In certain preferred embodiments the conversion is at least about 90%, and more preferably about 100%. Further in certain preferred embodiments, the conversion of the compound of formula (I) to produce a compound of formula (II) is conducted under conditions effective to provide a formula (II) selectivity of at least about 25%, more preferably at least about 40%, more preferably at least about 70%, and even more preferably at least about 90%.

This reaction step can be carried out in the liquid phase or in the gas phase, or in a combination of gas and liquid phases, and it is contemplated that the reaction can be carried out batch wise, continuous, or a combination of these.

A. LIQUID PHASE DEHYDROHALOGENATION

One preferred reaction step may be described, by way of illustration but not necessarily by way of limitation, by the following reaction equation in connection with embodiments in which the compound of formula (I) is 1,1,1,2,3 pentafluoropropane and the dehydrohalogenating agent is potassium hydroxide (KOH):



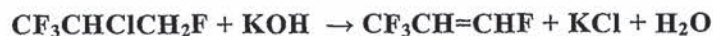
In such embodiments the KOH is preferably provided as an aqueous solution comprising from about 10% to about 50% by weight KOH, more preferably from about 20% to about 30% by weight.

5 In certain preferred embodiments, the KOH solution is brought to a relatively cool temperature, preferably from about -10°C to about 10°C, preferably about 0°C and introduced into a reaction vessel. The appropriate amount of formula (I) compound, which is preferably from about 1 to about 100 mole%, preferably, 0.9 to about 10 mole %, is then added to the reaction vessel. The reaction mixture is gradually heated, preferably with the addition of kinetic
10 energy (agitation or stirring) to from about 40°C to about 80°C, more preferably from about 50°C to about 60°C. Since the preferred reaction is exothermic, the temperature of the reaction mixture may be allowed to increase to a temperature of from about 60°C to about 95°C more preferably from about 65°C to about 75°C. The reaction pressure in such embodiments may vary, depending on
15 particular processing parameters of each application, but in certain embodiments ranges from about 0 to about 200 psig during the course of the reaction. In certain embodiments the reaction the exothermic heat of reaction is removed (such as by cooling) from the reaction mixture so as to maintain the reaction temperature in the range first mentioned above. The overall reaction time in
20 certain preferred embodiments is from about 5 to about 40 hours, more preferably from about 10 to about 30 hours, and even more preferably for about 20 hours.

After the desired reaction time, the reaction mixture is preferably cooled to facilitate collection of the reaction product, for example to about 20°C to about

down to 40°C. Preferably, the conversion, and selectivity to HFO-1234, and preferably HFO-1234yf, are each at least about 90% and more preferably at least about 95%.

Another preferred reaction step may be described, by way of illustration but not necessarily by way of limitation, by the following reaction equation in connection with embodiments in which the compound of formula (I) is 1,1,1,3-tetrafluoro-2-chloropropane and the dehydrohalogenating agent is potassium hydroxide (KOH):



In such embodiments the KOH is preferably provided as an aqueous solution comprising from about 10% to about 50% by weight KOH, more preferably from about 15% to about 25% by weight, with or without Crown ether. The appropriate amount of formula (I) compound, which is preferably from about 5 to about 9 mole, is then added to the reaction vessel. The reaction mixture is gradually heated, preferably with the addition of kinetic energy (agitation or stirring) to from about 40°C to about 80°C, more preferably from about 40°C to about 60°C at an overall reaction time of from about 2 to about 10 hours, more preferably from about 4 to about 8 hours, and even more preferably for about 6 hours. After the designated reaction time, the reaction mixture is preferably cooled to facilitate collection of the reaction product, for example to about -70°C. Preferably, the conversion of the reaction is at least about 50%, more preferably at least about 60%, and even more preferably at least about 70%.

The selectivity to HFO-1234ze is at least about 70%, more preferably at least about 75%, and even more preferably at least about 80%. Furthermore, in such embodiments it is preferred that of the HFO-1234ze produced, at least about 50%, more preferably at least about 75%, and even more preferably at least about 80% is trans-HFO-1234ze.

B. GAS PHASE DEHYDROHALOGENATION

Thus, it is contemplated that the dehydrohalogenation reaction step may be performed using a wide variety of process parameters and process conditions in view of the overall teachings contained herein, such as for example the liquid phase reaction described above. However, it is preferred in certain embodiments that this reaction step comprise a gas phase reaction, preferably in the presence of catalyst, preferably a metal catalyst, and even more preferably one or more transition metal-based catalysts (including in certain preferred embodiments transition metal halide catalysts), such as FeCl_3 , chromiumoxyfluoride, Ni (including Ni mesh), NiCl_2 , CrF_3 , and mixture thereof, supported or in bulk. Other catalysts include carbon-supported catalysts, antimony-based catalysts (such as Sb/Cl_5), aluminum-based catalyst (such as AlF_3 and Al_2O_3). It is expected that many other catalysts may be used depending on the requirements of particular embodiments, including for example palladium-based catalyst, platinum-based catalysts, rhodium-based catalysts and ruthenium-based catalysts. Of course, two or more any of these catalysts, or other catalysts not named here, may be used in combination.

In general it is preferred that the catalysts are fluorinated. In preferred embodiments, fluorination of the catalysts comprises exposing the catalyst to a stream of HF at about reaction temperature and pressure. The gas phase dehydrohalogenation reaction may be conducted, for example, by introducing a gaseous form of a compound of formula (I) into a suitable reaction vessel or reactor. Preferably the vessel is comprised of materials which are resistant to corrosion as Hastelloy, Inconel, Monel and/or fluoropolymers linings. Preferably the vessel contains catalyst, for example a fixed or fluid catalyst bed, packed with a suitable dehydrohalogenation catalyst, with suitable means to heat the reaction mixture to the desired reaction temperature.

While it is contemplated that a wide variety of reaction temperatures may be used, depending on relevant factors such as the catalyst being used and the most desired reaction product, it is generally preferred that the reaction temperature for the dehydrohalogenation step is from about 150°C to about 600°C, preferably about 200°C to about 550°C, and even more preferably from about 300°C to about 550°C.

In general it is also contemplated that a wide variety of reaction pressures may be used, depending again on relevant factors such as the specific catalyst being used and the most desired reaction product. The reaction pressure can be, for example, superatmospheric, atmospheric or under vacuum.

In certain embodiments, an inert diluent gas, such as nitrogen, may be used in combination with the compound of formula (I). When such a diluent is used, it is generally preferred that the compound of formula (I) comprise from

about 5 to greater than 95% by weight based on the combined weight of diluent and formula (I) compound.

It is contemplated that the amount of catalyst use will vary depending on the particular parameters present in each embodiment. In preferred embodiments, the contact time, which is expressed as the ratio of the volume of the catalyst (ml) to the total feed flow (ml/sec) is from about 0.1 seconds to about 1000 seconds, and preferably from about 2 seconds to about 120 seconds.

One preferred dehydrohalogenation reaction comprises a dehydrofluorination reaction. For example, for embodiments in which the desired product of formula (II) is HFO-1234yf, it is preferred that the compound of formula (I) comprises 1,1,1,2,3 pentafluoropropane. Applicants have found that in such embodiments it is preferred to use as the catalyst a nickel-based catalyst, a carbon based catalyst, or a combination of these. In highly preferred embodiments the catalyst is preferably a nickel mesh catalyst or nickel on a carbon support. In such embodiments it is also generally preferred to introduce to the reactor HF gas and inert gas, such as nitrogen, in a formula (I):HF:Inert volume ratio of from about 100:20:20 to about 100:80:80, with a ratio of about 100:40:40 being even more preferred. In addition, it is generally preferred to conduct at least a substantial portion of the reaction at a temperature of from about 450°C to about 600°C. In preferred aspects mbodiments, the contact time is from about 0.1 seconds to about 1000 seconds, and preferably from about 2 seconds to about 10 seconds.

Preferably in such dehydrofluorination embodiments, the conversion is at

least about 50%, more preferably at least about 65%, and even more preferably at least about 90%. Preferably, the selectivity to HFO-1234yf is at least about 70%, more preferably at least about 80% and more preferably at least about 90%.

Another preferred dehydrohalogenation reaction comprises a
5 dehydrochlorination reaction. For example, for embodiments in which the desired product of formula (II) is HFO-1234ze, it is preferred that the compound of formula (I) comprises 1,1,1,3-tetrafluoro-2-chloropropane. Applicants have found that in certain embodiments it is preferred to use for this reaction a nickel-based catalyst at a reaction temperature of from about 200°C to about 550°C,
10 more preferably from about 250°C to about 500°C, and even more preferably about 480°C. In certain other embodiments it is preferred to use for this reaction a activated carbon catalyst at a reaction temperature of from about 250°C to about 550°C, more preferably from about 300°C to about 550°C, and even more preferably about 515°C. In other embodiments it is preferred to use for this
15 reaction a catalyst comprising 3% palladium on carbon at a reaction temperature of from about 400°C to about 500°C, more preferably from about 425°C to about 475°C, and even more preferably about 550°C. In yet other embodiments it is preferred to use for this reaction a catalyst comprising 2% nickel on carbon at a reaction temperature of from about 400°C to about 500°C, more preferably from
20 about 450°C to about 500°C, and even more preferably about 485°C. In other embodiments it is preferred to use for this reaction a catalyst comprising chromiumoxyfluoride at a reaction temperature of from about 400°C to about 500°C, more preferably from about 400°C to about 450°C, and even more

preferably about 435°C.

In such dehydrochlorination embodiments it is an option to introduce to the reactor inert gas, such as nitrogen, in a formula (I):inert volume ratio of from about 100:25 to about 100:75, with a ratio of about 100:50 being even more preferred.

In preferred aspects of the dehydrochlorination embodiments, the contact time is from about 0.1 to about 1000 seconds, and preferably from about 3 to about 120 seconds.

Preferably in such dehydrofluorination embodiments, the conversion is at least about 50%, more preferably at least about 65%, and even more preferably at least about 90%. Preferably, the selectivity to HFO-1234ze, and even more preferably to trans-HFO-1234ze, is at least about 70%, more preferably at least about 80% and more preferably at least about 90%.

In general the direction of flow of the gaseous components may is not critical, but in certain preferred embodiments the process flow is in the down direction through a bed of the catalyst. Preferably before each cycle of use, the catalyst is dried, pre-treated and activated. It may also be advantageous in certain embodiments to periodically regenerate the catalyst after prolonged use while in place in the reactor. Pre-treatment may include heating the catalyst to about 250°C to about 430°C. with a stream of nitrogen or other inert gas. The catalyst may then be activated by treating it with a stream of HF diluted with a large excess of nitrogen gas in order to obtain high catalyst activity. Regeneration of the catalyst may be accomplished by any means known in the art such as, for

example, by passing nitrogen over the catalyst at temperatures of from about 100°C to about 400°C for from about 8 hours to about 3 days depending on the size of the reactor.

5

EXAMPLES

Certain features of the present invention are illustrated by the following examples, which should not be construed as limiting the claims in any way.

Examples 1 - 16

10

These examples illustrate gas phase dehydrofluorination of $\text{CF}_3\text{CHFCH}_2\text{F}$ (HFC-245eb) to $\text{CF}_3\text{CF}=\text{CH}_2$ (HFO-1234yf).

15

A 22-inch (1/2-inch diameter) Monel tube reactor is charged with 100 cc of catalyst, as specified in Table 1 below. A flow of 20 sccm of N_2 was maintained during the reaction. The reactor temperature is brought to the temperature indicated in the table. The HFC-245eb is passed through gas-flow controllers into a preheater maintained a temperature of about 300°C. The gas stream coming out of the preheater is passed through the catalyst bed at the desired temperature over a specified period of time. An on-line GC and a GCMS are used to analyze samples taken at the reactor exit line at regular time intervals.

20

Finally, the reactor effluent is introduced into a 20% KOH scrubber solution at about room temperature to remove acid HF formed in-situ during the reaction. The effluent from the scrubber solution is then condensed to collect the products.

The desired product $\text{CF}_3\text{CF}=\text{CH}_2$ (HFO-1234yf) is then isolated from the mixture by distillation.

The results are shown in Table 1 below.

Table 1: $\text{CF}_3\text{CHFCH}_2\text{F}$ (HFC-245eb) \rightarrow $\text{CF}_3\text{CF}=\text{CH}_2$ (1234yf)

Example# / Catalyst	T, °C	% Conversion of 245eb	% Selectivity to 1234yf	HFC- 245eb, gm/hr
Example 1/ Ni-mesh	495	36	100	10
Example 2/ Ni-mesh	525	67	100	10
Example 3/ Ni-mesh	565	89	78	10
Example 4/ Ni on carbon	495	63	94	10
Example 5/ Ni on carbon	525	79	84	10
Example 6/ Ni on carbon	565	100	69	8
Example 7/ Chromium Oxoxyfluoride	420	69	47	11

Example 8/ Chromium Oxoxyfluoride	440	78	43	10
Example 9/ Carbon	500	32	96	10
Example 10/ Carbon	550	69	86	11
Example 11/ Carbon	600	85	76	12
Example 12/ Pd/Carbon	450	56	58	5
Example 13/ Pd/Carbon	475	68	53	7
Example 15 4-6wt%FeCl ₃ /C	250	42	49	8
Example 16 4-6wt%FeCl ₃ /C	300	59	37	8

Examples 17 - 21

These examples illustrate gas phase dehydrochlorination of

5 $\text{CF}_3\text{CHClCH}_2\text{F}$ to $\text{CF}_3\text{CH=CHF}$ (HFO-1234ze).

A 22-inch (1/2-inch diameter) Monel tube reactor is charged with 50 cc of catalyst. A flow of 25 sccm of N₂ is maintained during the reaction. The reactor temperature is brought to the temperature indicated in the Table 2 below. The CF₃CHClCH₂F is passed through gas-flow controllers into a preheater maintained a temperature of about 300°C. The gas stream coming out of the preheater is passed through the catalyst bed at the desired temperature. Finally, the reactor effluent is introduced into a 20% KOH scrubber solution at about room temperature to remove acid HF or HCl formed in-situ during the reaction. The effluent from the scrubber solution is then condensed to collect the products. The desired product CF₃CH=CHF (1234ze) is then isolated from the mixture by distillation. The reaction produced selectivity to CF₃CH=CHF of from about 80% to about 87%, and to trans-CF₃CH=CHF of from about 87% to about 92%.

Table 2: CF₃CHClCH₂F → CF₃CH=CHF (1234yf)

Example# / Catalyst	T, °C
Example 17/ Ni-mesh	480
Example 18/ activated carbon	515
Example 19/ Chromium Oxoxyfluoride	436

Example 20/ Pd/Carbon	450
Example 21 2% Ni on Carbon	485

Example 22

This example illustrate liquid phase dehydrofluorination of $\text{CF}_3\text{CHFCH}_2\text{F}$ (HFC-245eb) to $\text{CF}_3\text{CF}=\text{CH}_2$ (HFO-1234yf). The compound of formula (I) $\text{CF}_3\text{CHFCH}_2\text{F}$ is stirred with 20% KOH solution in the presence or absence of 18-Crown ether at 50°C to synthesize $\text{CF}_3\text{CF}=\text{CH}_2$. A cleaned and leak tested 2 gallon autoclave is evacuated and then 2.5 L KOH water solution is charged into it. The KOH solution was cooled down to 0°C by a chiller. The autoclave is evacuated again and, using vacuum, 1.32Kg $\text{CF}_3\text{CFHCFH}_2$ is then charged to it. The sealed reactor is gradually heated with stirring to 55°C and then is heated by setting temperature at 55°C. After about 45 minutes reaction, the temperature increases to about 70°C by exothermic reaction (pressure is 165 psig). A cooling liquid is then applied to the reactor bring the temperature down to 57°C. Then the reaction is continued at 55°C for about 20 hours, and then the reaction mixture was cooled down to about 30°C and the gas product was transferred into a cylinder at dry ice-acetone temperature. About 1.1 Kg of $\text{CF}_3\text{CF}=\text{CH}_2$ with GC purity of about 98.6% was collected.

Example 23

This example illustrates the liquid phase dehydrochlorination of $\text{CF}_3\text{CHClCH}_2\text{F}$ to $\text{CF}_3\text{CH=CHF}$ (HFO-1234ze). About 150 g of 20% KOH solution, 1 g of 18-Crown ether, and 10 g of $\text{CF}_3\text{CHClCH}_2\text{F}$ are charged to a
5 teflon-lined 300 ml autoclave. The mixture is stirred at 50°C for 6 hours. The reaction progress is monitored by collecting samples and analyzing them by GC and MS in every 30 min. After the stipulated reaction period, the overhead gas mixture was transferred to a collection cylinder at -70°C. Analysis and overall
10 material balance confirms that 72% of the starting $\text{CF}_3\text{CHClCH}_2\text{F}$ is converted to $\text{CF}_3\text{CH=CHF}$ (HFO-1234ze) and the product selectivity was 81%, selectivity of 89% with respect to the trans isomer.

Example 24

This example illustrates the addition of ClF to $\text{CF}_3\text{CH=CH}_2$ in a liquid
15 phase reaction. Into a stirred tank 300 ml teflon-lined autoclave 10 g $\text{CF}_3\text{CH=CH}_2$ (0.104 mol) is charged. The reactor is subsequently cooled to -70°C for 1/2 hour and 6.35 g of ClF (0.116 mol) is added slowly at a rate of 2 g/15 min. After addition of ClF, the reaction mixture is stirred at -55°C for about 2 hours.
20 Then the temperature is raised to 20°C over a period of 1 hour under vigorous stirring. The mixture is stirred at this temperature for another 2 hours. The mixture is then cooled to -50°C, and 10 g of water are added to the reactor, and stirring continues for 15 additional minutes. The reactor temperature was then

brought back to 20°C. The gaseous products from the reactor are then transferred to a collection cylinder which is maintained at liquid nitrogen temperature. GC and MS analysis and material balance of the sample from the collection cylinder show that almost 100% of the starting $\text{CF}_3\text{CH}=\text{CH}_2$ is converted to $\text{CF}_3\text{CFCICH}_2\text{F}$ with almost 99% selectivity.

Example 25

This example illustrates the reaction of HF and Cl_2 with $\text{CF}_3\text{CH}=\text{CH}_2$ in a liquid phase reaction. It is an assumption that ClF is also generated in situ by the liquid phase reaction of HF and Cl_2 in the presence of transition metal halides such as FeCl_3 , TaCl_5 , TiCl_4 , SbCl_5 , SbCl_3 , and CrCl_3 , SbF_3 , AlF_3 , and CrF_3 . In a first reaction vessel, HF, Cl_2 and metal chloride salts are stirred with $\text{CF}_3\text{CH}=\text{CH}_2$ at -40°C for 2 hours to synthesize 48% $\text{CF}_3\text{CHCICH}_2\text{F}$ and 20% $\text{CF}_3\text{CHCICH}_2\text{Cl}$, 10% $\text{CF}_3\text{CHCICH}_2\text{Cl}$, 8% $\text{CF}_3\text{CH}_2\text{CH}_2\text{F}$, and 5% $\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$ at a $\text{CF}_3\text{CH}=\text{CH}_2$ conversion level of 100%.

The same reaction is also performed using two autoclaves in two steps. In the first step, ClF is synthesized by the liquid phase reaction of HF and Cl_2 in the presence of transition metal halide such as SbF_5 in an autoclave which is then subsequently transferred to a second autoclave containing $\text{CF}_3\text{CH}=\text{CH}_2$ at about -40°C. Selectivity to $\text{CF}_3\text{CHCICH}_2\text{F}$ is about 80%.

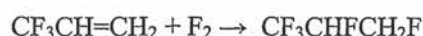
Example 26

This example illustrates the addition of F_2 to $CF_3CH=CH_2$ in a liquid phase reaction. About 5 - 100 wt% F_2 in nitrogen is bubbled through 125 g of liquid trifluoropropylene (TFP) in a stirred Hastrelloy C reactor at about -20°C to about -55°C for about 1 hour in the presence of HF as the solvent. A 1 gallon Parr reactor is first charged with a relatively inert solvent, HF, to help with heat transfer and dilution of the organic. Then 125 grams of TFP is added batch wise to the reactor. The reaction mixture is continuously mixed and cooled to the desired temperature. Then the F_2 feed (10wt%), diluted with N_2 (90 wt%), is introduced continuously directly into the reaction mixture through a dip tube until about 90% of the stoichiometric amount needed to convert all the TFP that is added. The reactor temperature and pressure are controlled automatically at the desired set points of between -20 to -55°C and a constant pressure of 40 psig. The temperatures are chosen to minimize the amount of TFP that would exit the reactor with the N_2 diluent. The gases exiting the reactor are passed through a caustic scrubber carboy and an activated alumina column to remove acidity, then a dri-rite column to remove moisture, and finally the organic is collected in a DIT. When the desired amount of F_2 is added the reaction liquid is sampled. The sample is absorbed in H_2O and the organic is recovered by phase separation. The organic is then analyzed by GC and GC/MS. The remaining material in the reactor is boiled off through the scrubbing system and the organic is collected in the DIT

and analyzed by GC and GC/MS. The analyses are used to determine that the reaction has an overall selectivity to $\text{CF}_3\text{CHFCH}_2\text{F}$ of about 36-45%.

Example 27

5 This example illustrates addition of F_2 to $\text{CF}_3\text{CH}=\text{CH}_2$ in a gas phase reaction, which is illustrated by the following reaction scheme:



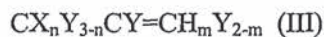
10 The same apparatus as described in Example 25 is used, except that gaseous TFP and 10% F_2 (90% dilution w/ N_2) are fed into the Parr reactor via a common dip tube. TFP is fed at a 50% stoichiometric excess. The reactor is kept at -18°C and at atmospheric pressure. The reactor effluent is passed through a D1T, which collected most of the organic. Only a couple of grams of vapor are left in the Parr reactor at the end of the experiment. GC analysis of the material indicated about 10% conversion of the propylene. The selectivity to
15 $\text{CF}_3\text{CHFCH}_2\text{F}$ is about 52% based on GC area percentage.

 Having thus described a few particular embodiments of the invention, various alterations, modifications, and improvements will readily occur to those skilled in the art. Such alterations, modifications, and improvements, as are made obvious by this disclosure, are intended to be part of this description
20 though not expressly stated herein, and are intended to be within the spirit and scope of the invention. Accordingly, the foregoing description is by way of example only, and not limiting. The invention is limited only as defined in the following claims and equivalents thereto.

CLAIMS

What is claimed is:

- 5 1. A method of preparing fluorinated organic compounds comprising
converting at least one compound of formula (I):
- $$\text{CF}_3\text{CHXCH}_2\text{X} \quad (\text{I})$$
- to at least one compound of formula (II)
- $$\text{CF}_3\text{CZCHZ} \quad (\text{II})$$
- 10 where X is independently Cl or F, and Z is independently is H or F.
2. The method of claim 1 wherein said compound of formula (I) is formed by
halogen addition comprising contacting a fluorinated C3 olefin with a
halogen addition agent under conditions effective to produce a compound of
formula (I).
- 15 3. The method of claim 2 wherein said halogen addition agent comprises
fluorine gas.
4. The method of claim 3 wherein said halogen addition step comprises a gas
phase reaction.
5. The method of claim 2 wherein said halogen addition agent comprises ClF.
- 20 6. The method of claim 2 wherein said halogen addition step is carried out at a
temperature of from about -90°C to about 50°C.
7. The method of claim 2 wherein said fluorinated C3 olefin comprises a
compound of formula (III)



where each X is independently Cl or F, each Y is independently H, Cl or F,
n is 1, 2 or 3, and m is 1 or 2.

8. The method of claim 7 wherein said compound of formula (III) comprises a
5 compound of formula (IIIA)



9. The method of claim 8 wherein said compound of formula I comprises
 $\text{CF}_3\text{CHFCH}_2\text{F}$.
10. The method of claim 8 wherein said halogen addition agent is a compound
10 of formula X_mY_{2-m} where X, Y and m are as described above.
11. The method of claim 8 wherein said halogen addition agent is selected from
the group consisting of ClF, Cl_2 , F_2 , HF and combinations of these.
12. The method of claim 10 wherein said halogen addition agent comprises F_2 ,
said compound of formula (III) comprises 3,3,3-trifluoro-1-propene, and
15 said compound of formula (I) comprises $\text{CF}_3\text{CHFCH}_2\text{F}$.
13. The method of claim 1 wherein said converting step comprises introducing
said compound of formula (I) to a reaction system under conditions
effective to convert at least about 50% of said compound of formula (I).
14. The method of claim 13 wherein said reaction system comprises catalyst.
- 20 15. The method of claim 1 wherein said converting step comprises introducing
said compound of formula (I) to a reaction system under conditions
effective to produce a reaction product having at least about 70% selectivity
to compound(s) of formula (II).

16. The method of claim 15 wherein said compound(s) of formula (II) include tetrafluoropropene.
17. The method of claim 16 wherein said compound(s) of formula (II) include HFO-1234yf.
- 5 18. The method of claim 16 wherein said compound(s) of formula (II) include HFO-1234ze.
19. The method of claim 1 wherein said compound of formula (I) is 1,1,1,2,3 pentafluoropropane and said converting step comprises exposing said compound to a dehydrohalogenation agent comprising potassium hydroxide (KOH).
- 10 20. The method of claim 19 wherein said compound of formula (II) comprises HFO-1234yf.
21. The method of claim 20 wherein said converting step is carried out under conditions effective to convert at least about 80% of said 1,1,1,2,3 pentafluoropropane and to provide a selectivity to HFO-1234yf of at least about 90%.
- 15 22. The method of claim 19 wherein said compound of formula (I) comprises 1,1,1,3-tetrafluoro-2-chloropropane and said compound of formula (II) comprises HFO-1234ze.
- 20 23. The method of claim 22 wherein said converting step is carried out under conditions effective to convert at least about 50% of said 1,1,1,3-tetrafluoro-2-chloropropane and to provide a selectivity to HFO-1234ze of at least about 70%.

24. The method of claim 1 wherein said contacting step comprises conducting at least a portion of said contacting step at a temperature of from about 250°C to about 600°C.
- 5 25. The method of claim 1 wherein said contacting step comprises conducting at least a portion of said contacting step at a pressure of from about 10 to about 120 psia.
26. The method of claim 25 wherein said contacting step comprises conducting at least a portion of said contacting step in the gas phase and in the presence of a catalyst.
- 10 27. The method of claim 26 wherein said catalyst comprises nickel.
28. The method of claim 27 wherein the compound of formula (I) comprises 1,1,1,3-tetrafluoro-2-chloropropane and the compound of formula (II) comprises HFO-1234ze.
- 15 29. The method of claim 25 wherein at least a portion of said converting step is conducted at a temperature of from about 400°C to about 550°C.
30. The method of claim 29 wherein said catalyst comprises activated carbon.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/043053

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C17/25 C07C21/18 C07C17/04 C07C19/10 C07C19/08

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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, CHEM ABS Data, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y		1-30
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

27 March 2007

Date of mailing of the international search report

11/04/2007

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Seufert, Gudrun

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/043053

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	----- -----	1-18, 24-26, 29,30
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/043053

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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