

HALOGENATED PERFLUOROALIPHATIC COMPOUNDS AND METHODS OF MAKING AND USING THE SAME

FIELD

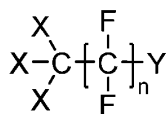
[0001] The present disclosure is directed to a method for making halogenated perfluoroaliphatic compounds as well as methods for making products therefrom.

BACKGROUND

[0002] 1,3-Hexafluorobutadiene (or “HFBD”) is used as an etchant in the microelectronics industry. This etchant is considered environmentally friendly due to its low greenhouse warming potential (GWP = 0). It is used in multiple etchant processes, such as reactive ion etching (RIE), deep reactive ion etching (DRIE), plasma-enhanced chemical vapor deposition (PECVD) and chamber cleaning. Methods for making HFBD exist; however, they rely on utilizing multi-step protocols or utilizing reagents and/or reaction conditions that are not desirable from a safety perspective. Furthermore, methods for arriving at starting materials that can readily be converted to products like HFBD are limited and/or are used to make starting materials that require harsh/undesirable reaction conditions to convert the starting materials to the desired product. There exists a need in the art for a new method that can be readily applied to making a variety of perfluoroaliphatic starting materials that can be used to arrive at products like HFBD and/or other fluorinated compounds.

SUMMARY

[0003] Disclosed herein is a method for making a halogenated perfluoroaliphatic compound, comprising: exposing a fluorine-containing compound having a structure according to Formula I to a halogen-based reagent at a reaction temperature ranging from greater than ambient temperature to a temperature of 750 °C to provide a reaction mixture; and isolating the halogenated perfluoroaliphatic compound from the reaction mixture; wherein Formula I is



Formula I

wherein each X independently is selected from H, F, Br, or -CH₂OH; n is an integer selected from 1 to 25; and Y is selected from H, -C(O)OH, -SO₃H, -SH; or -C(O)R or -[CH₂]_mOR, wherein R is hydrogen, aliphatic, or cycloaliphatic, and m is an integer selected from 1 to 10; or -[CH₂]NR^aR^b,

wherein each of R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, aromatic, or an organic functional group; or -C(O)OR', -C(O)OC(O)R', -[CH₂]_mO-[CH₂]_mR' or -S-SR', wherein R' is a haloaliphatic group and m is an integer selected from 1 to 10; provided that (i) if Y is -[CH₂]_mOR, wherein R is H and m is 1, (ii) n is 3, and (iii) two X groups are F and one X group is H, then the halogen-based reagent is not, or is other than, Cl₂.

[0004] Also disclosed herein is a method for making 1,3-hexafluorobutadiene, comprising exposing 1,4-dibromo-1,1,2,2,3,3,4,4-octafluorobutane or 1,4-dichloro-1,1,2,2,3,3,4,4-octafluorobutane to an alkyl magnesium compound, an aromatic magnesium compound, or alkyl lithium compound comprising an alkyl group comprising five or more carbon atoms.

[0005] The foregoing and other objects, features, and advantages of the present disclosure will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 is an ¹⁹F nuclear magnetic resonance (NMR) spectrum of 1,4-dibromooctafluorobutane (or "DBOFB") made according to an aspect of the present disclosure.

[0007] FIG. 2A is an ¹H NMR spectrum of 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (or "BOFB") made according to an aspect of the present disclosure.

[0008] FIG. 2B is an ¹⁹F NMR spectrum of BOFB made according to an aspect of the present disclosure.

[0009] FIG. 3A is an ¹⁹F NMR spectrum of a reaction mixture comprising DBOFB, BOFB, and 1,2-dibromotetrafluoroethane (or "DBTFE") made according to an aspect of the present disclosure.

[0010] FIG. 3B is an ¹H NMR spectrum of a reaction mixture comprising DBOFB, BOFB, and DBTFE obtained according to an aspect of the present disclosure.

[0011] FIG. 4A is an ¹⁹F NMR spectrum of a reaction mixture comprising DBOFB, BOFB, and DBTFE obtained according to another aspect of the present disclosure.

[0012] FIG. 4B is an ¹H NMR spectrum of a reaction mixture comprising DBOFB, BOFB, and DBTFE obtained according to another aspect of the present disclosure.

[0013] FIG. 5A is an ¹⁹F NMR spectrum of a reaction mixture comprising DBOFB, BOFB, DBTFE, and octafluorobutane (or "OFB") obtained according to an aspect of the present disclosure.

[0014] FIG. 5B is an ^1H NMR spectrum of a reaction mixture comprising DBOFB, BOFB, DBTFE, and octafluorobutane (or "OFB") obtained according to an aspect of the present disclosure.

[0015] FIG. 6A is an ^{19}F NMR spectrum of a reaction mixture comprising 1,6-dibromodecafluorohexane (or "DBDFH"), 1-bromo-2,2,3,3,4,4,5,5,6,6-dodecafluorohexane (or "BDFH"), and 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1-heptanol (or "DFHO") obtained according to an aspect of the present disclosure.

[0016] FIG. 6B is an ^1H NMR spectrum of a reaction mixture comprising DBDFH, BDFH, and DFHO obtained according to an aspect of the present disclosure.

[0017] FIG. 7A is an ^{19}F NMR spectrum of a reaction mixture comprising DBDFH, BDFH, and DFHO obtained according to another aspect of the present disclosure.

[0018] FIG. 7B is an ^1H NMR spectrum of a reaction mixture comprising DBDFH, BDFH, and DFHO obtained according to another aspect of the present disclosure.

[0019] FIG. 8A is an ^1H NMR spectrum of a reaction mixture comprising DBTFE and 1-bromo-1,1,2,2-tetrafluoroethane (or "BTFE") obtained according to an aspect of the present disclosure.

[0020] FIG. 8B is an ^{19}F NMR spectrum of a reaction mixture comprising DBTFE and BTFE obtained according to an aspect of the present disclosure, including an expanded view of certain peaks.

[0021] FIG. 8C is the ^{19}F NMR spectrum of FIG. 8B without the expanded view.

[0022] FIG. 9 is an ^{19}F NMR spectrum of 1,3-Hexafluorobutadiene (or "HFBD").

DETAILED DESCRIPTION

[0023] Overview of Terms

[0024] The following explanations of terms are provided to better describe the present disclosure and to guide those of ordinary skill in the art in the practice of the present disclosure. As used herein, "comprising" means "including" and the singular forms "a" or "an" or "the" include plural references unless the context clearly dictates otherwise. The term "or" refers to a single element of stated alternative elements or a combination of two or more elements, unless the context clearly indicates otherwise.

[0025] Although the steps of some of the disclosed methods are described in a particular, sequential order for convenient presentation, it should be understood that this manner of description encompasses rearrangement, unless a particular ordering is required by specific

language set forth below. For example, steps described sequentially may in some cases be rearranged or performed concurrently. Additionally, the description sometimes uses terms like “produce” and “provide” to describe the disclosed methods. These terms are high-level abstractions of the actual steps that are performed. The actual steps that correspond to these terms will vary depending on the particular implementation and are readily discernible by one of ordinary skill in the art.

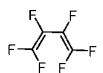
[0026] Unless explained otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. Although methods and compounds similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and compounds are described below. The compounds, methods, and examples are illustrative only and not intended to be limiting, unless otherwise indicated. Other features of the disclosure are apparent from the following detailed description and the claims.

[0027] Unless otherwise indicated, all numbers expressing quantities of components, molecular weights, percentages, temperatures, times, and so forth, as used in the specification or claims are to be understood as being modified by the term “about.” Accordingly, unless otherwise indicated, implicitly or explicitly, the numerical parameters set forth are approximations that can depend on the desired properties sought and/or limits of detection under standard test conditions/methods. When directly and explicitly distinguishing disclosed aspects from discussed prior art, the numbers are not approximates unless the word “about” is recited. Furthermore, not all alternatives recited herein are equivalents.

[0028] A person of ordinary skill in the art would recognize that the definitions provided below and the compounds and formulas included herein are not intended to include impermissible substitution patterns (*e.g.*, methyl substituted with 5 different groups, and the like). Such impermissible substitution patterns are easily recognized by a person of ordinary skill in the art. Any functional group disclosed herein and/or defined above can be substituted or unsubstituted, unless otherwise indicated herein.

[0029] To facilitate review of the various aspects of the disclosure, the following explanations of specific terms and abbreviations are provided:

[0030] **1,3-Hexafluorobutadiene (HFBD):** A compound having a formula C_4F_6 and the structure shown below



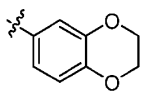
[0031] **Aliphatic:** A hydrocarbon group having at least one carbon atom to 50 carbon atoms (C_{1-50}), such as one to 25 carbon atoms (C_{1-25}), or one to ten carbon atoms (C_{1-10}), and which includes alkanes (or alkyl), alkenes (or alkenyl), alkynes (or alkynyl), further including straight- and branched-chain arrangements, and all stereo and position isomers as well.

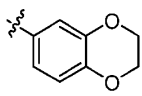
[0032] **Alkenyl:** An unsaturated monovalent hydrocarbon having at least two carbon atoms to 50 carbon atoms (C_{2-50}), such as two to 25 carbon atoms (C_{2-25}), or two to ten carbon atoms (C_{2-10}), and at least one carbon-carbon double bond, wherein the unsaturated monovalent hydrocarbon can be derived from removing one hydrogen atom from one carbon atom of a parent alkene. An alkenyl group can be branched, straight-chain, *cis*, or *trans* (e.g., *E* or *Z*).

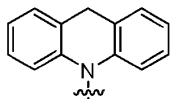
[0033] **Alkyl:** A saturated monovalent hydrocarbon having at least one carbon atom to 50 carbon atoms (C_{1-50}), such as one to 25 carbon atoms (C_{1-25}), or one to ten carbon atoms (C_{1-10}), wherein the saturated monovalent hydrocarbon can be derived from removing one hydrogen atom from one carbon atom of a parent compound (e.g., alkane). An alkyl group can be branched or straight-chain.

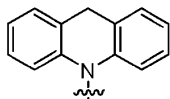
[0034] **Alkynyl:** An unsaturated monovalent hydrocarbon having at least two carbon atoms to 50 carbon atoms (C_{2-50}), such as two to 25 carbon atoms (C_{2-25}), or two to ten carbon atoms (C_{2-10}), and at least one carbon-carbon triple bond, wherein the unsaturated monovalent hydrocarbon can be derived from removing one hydrogen atom from one carbon atom of a parent alkyne. An alkynyl group can be branched or straight-chain.

[0035] **Aromatic:** A cyclic, conjugated group or moiety of, unless specified otherwise, from 5 to 15 ring atoms having a single ring (e.g., phenyl) or multiple condensed rings in which at least one ring is aromatic (e.g., naphthyl, indolyl, or pyrazolopyridinyl); that is, at least one ring, and optionally multiple condensed rings, have a continuous, delocalized π -electron system. Typically, the number of out of plane π -electrons corresponds to the Hückel rule ($4n + 2$). The point of attachment to the parent structure typically is through an aromatic portion of the condensed ring



system. For example, . However, in certain examples, context or express disclosure may indicate that the point of attachment is through a non-aromatic portion of the condensed ring



system. For example, . An aromatic group or moiety may comprise only carbon atoms in the ring, such as in an aryl group or moiety, or it may comprise one or more ring carbon atoms and one or more ring heteroatoms comprising a lone pair of electrons (e.g., S, O, N, P, or Si), such as in a heteroaryl group or moiety. Aromatic groups may be substituted with one or more

groups other than hydrogen, such as aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group.

[0036] **Aryl:** An aromatic carbocyclic group comprising at least five carbon atoms to 15 carbon atoms (C_5 - C_{15}), such as five to ten carbon atoms (C_5 - C_{10}), having a single ring or multiple condensed rings, which condensed rings can or may not be aromatic provided that the point of attachment to a remaining position of the compounds disclosed herein is through an atom of the aromatic carbocyclic group. Aryl groups may be substituted with one or more groups other than hydrogen, such as aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group.

[0037] **Brominated Perfluoroaliphatic Compound:** A compound comprising a plurality of carbon-fluorine bonds and at least one carbon-bromine bond. In some aspects, the brominated perfluoroaliphatic compound can further comprise a C-H bond. Brominated perfluoroaliphatic compounds can be saturated or unsaturated and, within the context of the present disclosure, comprise a linear, acyclic perfluoroaliphatic carbon chain.

[0038] **Cycloaliphatic:** A cyclic hydrocarbon group having at least three carbon atoms to 50 carbon atoms (C_{1-50}), such as three to 25 carbon atoms (C_{1-25}), or three to ten carbon atoms (C_{1-10}), and which includes cycloalkanes (or cycloalkyl), cycloalkenes (or cycloalkenyl), cycloalkynes (or cycloalkynyl), and further including branched-cyclic arrangements, and all stereo and position isomers as well.

[0039] **Cycloalkyl:** A cyclic saturated monovalent hydrocarbon having at least three carbon atoms to 50 carbon atoms (C_{1-50}), such as three to 25 carbon atoms (C_{1-25}), or three to ten carbon atoms (C_{1-10}), wherein the saturated monovalent hydrocarbon can be derived from removing one hydrogen atom from one carbon atom of a parent compound (e.g., cycloalkane). Cycloalkyl also includes branched-cyclic arrangements.

[0040] **Cycloalkenyl:** A cyclic unsaturated monovalent hydrocarbon having at least four carbon atoms to 50 carbon atoms (C_{2-50}), such as four to 25 carbon atoms (C_{2-25}), or four to ten carbon atoms (C_{2-10}), and at least one carbon-carbon double bond, wherein the unsaturated monovalent hydrocarbon can be derived from removing one hydrogen atom from one carbon atom of a parent cycloalkene. A cycloalkenyl group can be *cis* or *trans* (e.g., *E* or *Z*), and includes branched-cyclic arrangements.

[0041] **Cycloalkynyl:** A cyclic unsaturated monovalent hydrocarbon having at least four carbon atoms to 50 carbon atoms (C_{2-50}), such as four to 25 carbon atoms (C_{2-25}), or four to ten carbon atoms (C_{2-10}), and at least one carbon-carbon triple bond, wherein the unsaturated monovalent

hydrocarbon can be derived from removing one hydrogen atom from one carbon atom of a parent cycloalkyne. Cycloalkynyl also includes branched-cyclic arrangements.

[0042] **Cyclohaloaliphatic:** A cycloaliphatic group wherein one or more hydrogen atoms, such as one to 10 hydrogen atoms, independently is replaced with a halogen atom, such as fluoro, bromo, chloro, or iodo.

[0043] **Cycloheteroaliphatic:** A cycloaliphatic group comprising at least one heteroatom to 20 heteroatoms, such as one to 15 heteroatoms, or one to 5 heteroatoms, which can be selected from, but not limited to oxygen, nitrogen, sulfur, silicon, boron, selenium, phosphorous, and oxidized forms thereof within the group.

[0044] **Fluorine-Containing Compound:** A linear compound comprising at least two carbon-fluorine bonds and having a structure according to Formula I disclosed herein.

[0045] **Halo (or halide or halogen):** Fluoro, chloro, bromo, or iodo.

[0046] **Haloaliphatic:** An aliphatic group wherein one or more hydrogen atoms, such as one to 10 hydrogen atoms, independently is replaced with a halogen atom, such as fluoro, bromo, chloro, or iodo.

[0047] **Halogenated Perfluoroaliphatic Compound:** A compound comprising a plurality of carbon-fluorine bonds and at least one carbon-halogen bond. In some aspects, the halogenated perfluoroaliphatic compound can further comprise a C-H bond. Halogenated perfluoroaliphatic compounds can be saturated or unsaturated and, within the context of the present disclosure, comprise a linear, acyclic perfluoroaliphatic carbon chain. In representative aspects, the at least one carbon-halogen bond of the halogenated perfluoroaliphatic compound is a bond between a carbon atom and a halogen other than fluorine.

[0048] **Heat Source:** A type of energy source that is capable of providing a reaction temperature ranging from a temperature greater than ambient temperature (e.g., above 25 °C) to a temperature of 750 °C. Exemplary heat sources can include an oven, a heat plate, a heated tube or other reaction vessel, an autoclave, or the like, unless otherwise indicated.

[0049] **Heteroaliphatic:** An aliphatic group comprising at least one heteroatom to 20 heteroatoms, such as one to 15 heteroatoms, or one to 5 heteroatoms, which can be selected from, but not limited to oxygen, nitrogen, sulfur, silicon, boron, selenium, phosphorous, and oxidized forms thereof within the group. Alkoxy (e.g., -O-aliphatic), ether (e.g., -aliphatic-O-aliphatic, -aliphatic-O-aromatic, -aromatic-O-aliphatic, or -aromatic-O-aromatic), amino (e.g., -NR^aR^b, wherein each of R^a and R^b independently is selected from hydrogen, aliphatic,

heteroaliphatic, haloaliphatic, aromatic, or an organic functional group), disulfide (e.g., $-SSR^a$, wherein R^a is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, aromatic, or an organic functional group), peroxy (e.g., $-O-OR^a$ wherein R^a is hydrogen, aliphatic, heteroaliphatic, haloaliphatic, aromatic, or an organic functional group), and thioether (e.g., $-S$ -aliphatic or $-S$ -aromatic, such as $-S$ -alkyl, $-S$ -alkenyl, $-S$ -alkynyl, $-S$ -aryl, or $-S$ -heteroaryl; or $-S$ -aliphatic- S -aliphatic, $-S$ -aliphatic- S -aromatic, $-S$ -aromatic- S -aliphatic, or $-S$ -aromatic- S -aromatic) groups are exemplary (but non-limiting) examples of heteroaliphatic.

[0050] **Heteroaryl:** An aryl group comprising at least one heteroatom to six heteroatoms, such as one to four heteroatoms, which can be selected from, but not limited to oxygen, nitrogen, sulfur, silicon, boron, selenium, phosphorous, and oxidized forms thereof within the ring. Such heteroaryl groups can have a single ring or multiple condensed rings, wherein the condensed rings may or may not be aromatic and/or contain a heteroatom, provided that the point of attachment is through an atom of the aromatic heteroaryl group. Heteroaryl groups may be substituted with one or more groups other than hydrogen, such as aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group.

[0051] **Heteroatom:** An atom other than carbon or hydrogen, such as (but not limited to) oxygen, nitrogen, sulfur, silicon, boron, selenium, or phosphorous. In particular disclosed aspects, such as when valency constraints do not permit, a heteroatom does not include a halogen atom.

[0052] **Organic Functional Group:** A functional group that may be provided by any combination of aliphatic, heteroaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, and/or haloaliphatic groups, or that may be selected from, but not limited to, aldehyde (i.e., $-C(O)H$); aroxy (i.e., $-O$ -aromatic); acyl halide (i.e., $-C(O)X$, wherein X is a halogen, such as Br, F, I, or Cl); halogen; nitro (i.e., $-NO_2$); cyano (i.e., $-CN$); azide (i.e., $-N_3$); carboxyl (i.e., $-C(O)OH$); carboxylate (i.e., $-C(O)O^-$ or salts thereof, wherein the negative charge of the carboxylate group may be balanced with an M^+ counterion, wherein M^+ may be an alkali ion, such as K^+ , Na^+ , Li^+ ; an ammonium ion, such as $^+N(R^b)_4$ where R^b is H, aliphatic, heteroaliphatic, haloaliphatic, or aromatic; or an alkaline earth ion, such as $[Ca^{2+}]_{0.5}$, $[Mg^{2+}]_{0.5}$, or $[Ba^{2+}]_{0.5}$); amide (i.e., $-C(O)NR^aR^b$ or $-NR^aC(O)R^b$ wherein each of R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); ketone (i.e., $-C(O)R^a$, wherein R^a is selected from aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); carbonate (i.e., $-OC(O)OR^a$, wherein R^a is selected from aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); imine (i.e., $-C(=NR^a)R^b$ or $-N=CR^aR^b$, wherein R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic,

cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); azo (i.e., -N=NR^a wherein R^a is hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); carbamate (i.e., -OC(O)NR^aR^b, wherein each of R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); hydroxyl (i.e., -OH); thiol (i.e., -SH); sulfonyl (i.e., -SO₂R^a, wherein R^a is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); sulfonate (i.e., -SO₃⁻, wherein the negative charge of the sulfonate group may be balanced with an M⁺ counter ion, wherein M⁺ may be an alkali ion, such as K⁺, Na⁺, Li⁺; an ammonium ion, such as ⁺N(R^b)₄ where R^b is H, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, or aromatic; or an alkaline earth ion, such as [Ca²⁺]_{0.5}, [Mg²⁺]_{0.5}, or [Ba²⁺]_{0.5}); oxime (i.e., -CR^a=NOH, wherein R^a is hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); sulfonamide (i.e., -SO₂NR^aR^b or -N(R^a)SO₂R^b, wherein each of R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); ester (i.e., -C(O)OR^a or -OC(O)R^a, wherein R^a is selected from aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); thiocyanate (i.e., -S-CN or -N=C=S); thioketone (i.e., -C(S)R^a wherein R^a is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); thiocarboxylic acid (i.e., -C(O)SH, or -C(S)OH); thioester (i.e., -C(O)SR^a or -C(S)OR^a wherein R^a is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); dithiocarboxylic acid or ester (i.e., -C(S)SR^a wherein R^a is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); phosphonate (i.e., -P(O)(OR^a)₂, wherein each R^a independently is hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group; or wherein one or more R^a groups are not present and the phosphate group therefore has at least one negative charge, which can be balanced by a counterion, M⁺, wherein each M⁺ independently can be an alkali ion, such as K⁺, Na⁺, Li⁺; an ammonium ion, such as ⁺N(R^b)₄ where R^b is H, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, or aromatic; or an alkaline earth ion, such as [Ca²⁺]_{0.5}, [Mg²⁺]_{0.5}, or [Ba²⁺]_{0.5}); phosphate (i.e., -O-P(O)(OR^a)₂, wherein each R^a independently is hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group; or wherein one or more R^a groups are not present and the phosphate group therefore has at least one negative

charge, which can be balanced by a counterion, M^+ , wherein each M^+ independently can be an alkali ion, such as K^+ , Na^+ , Li^+ ; an ammonium ion, such as $^+N(R^b)_4$ where R^b is H, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, or aromatic; or an alkaline earth ion, such as $[Ca^{2+}]_{0.5}$, $[Mg^{2+}]_{0.5}$, or $[Ba^{2+}]_{0.5}$; silyl ether (i.e., $-OSiR^aR^b$, wherein each of R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); sulfinyl (i.e., $-S(O)R^a$, wherein R^a is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, aromatic, or an organic functional group); thial (i.e., $-C(S)H$); or combinations thereof.

[0053] Introduction

[0054] Disclosed herein is a method for converting fluorine-containing compounds (used as starting materials) to halogenated perfluoroaliphatic compounds comprising at least one halogen atom other than fluorine (e.g., Br, I, or Cl). In particular aspects of the disclosure, the method is directed to making brominated perfluoroaliphatic compounds, chlorinated perfluoroaliphatic compounds, iodinated perfluoroaliphatic compounds, or perfluoroaliphatic compounds. The method is a one-step process that can be used to convert myriad different fluorine-containing compounds to halogenated perfluoroaliphatic compounds in high yield using efficient and cost-effective reagents. While certainly not the only advantage, the disclosed method provides a single-step protocol to convert myriad different starting materials to halogenated versions of the starting material using gas phase reaction conditions. In particular aspects of the disclosure, the products obtained with the method can be converted to other valuable products, such as HFBD, fluorotelomers, and the like. In an independent aspect of the disclosure, the halogenated perfluoroaliphatic compound is not, or is other than, 1-chloro-1,1,2,2,3,3,4,4-octafluorobutane.

[0055] The disclosed method provides easy access to numerous halogenated perfluorinated compounds utilizing a combination of starting materials and chemical transformations of these starting material not known in the art prior to the present disclosure. While those in the art have shown the ability to convert starting materials, such as a perfluorinated acyl fluoride to a halogenated perfluoroaliphatic product, this conversion was not demonstrated using the types of fluorine-containing compounds disclosed herein. And, while those in the art have shown that the fluorinated primary alcohol 2,2,3,3,4,4,5,5-octafluoropentanol-1-ol can be converted to a monochlorinated product, this method is not conducive to obtaining other halogenated products (e.g., brominated products) and is not translated to other alcohols as evidenced by the fact that the method did not convert 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol-1-ol to the chlorinated product. In contrast to these prior methods, the present disclosure describes a method that is applicable

and reproducible across a wide variety of starting materials. The desired halogenated perfluoroaliphatic compounds are obtained in one-step using a safe, good yielding procedure.

[0056] **Method**

[0057] In aspects of the present disclosure, a method is described that converts a fluorine-containing compound (as a starting material) to halogenated perfluoroaliphatic compound (as a product). In particular aspects of the method, the fluorine-containing compound is a n H-perfluoro compound, wherein n represents the number of carbon atoms present and is an integer ranging from 1 to 25, such as 1 to 22, or 1 to 20, or 1 to 18, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25. In particular aspects of the disclosure, the method is used to make 1, n -dibromoperfluorocarbons, wherein n represents the number of carbon atoms present in the product and is an integer ranging from 1 to 25, such as 1 to 22, or 1 to 20, or 1 to 18, or 1 to 16, or 1 to 14, or 1 to 12, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25.

[0058] The method comprises exposing the fluorine-containing compound to a halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂, etc.) in the presence of an energy source, such as a light source, a heat source, or a combination thereof. In particular aspects of the disclosure, the energy source can be a light source that is capable of producing UV light, such as light having a wavelength ranging from 10 nm to 400 nm, such as 100 nm to 400 nm, or 150 nm to 400 nm, or 200 nm to 400 nm, or 250 nm to 400 nm, or 300 nm to 400 nm. In some aspects of the disclosure, the energy source can be a heat source capable of providing a reaction temperature ranging from a temperature greater than ambient temperature (e.g., above 25 °C) to a temperature of 750 °C, such as 50 °C to 750 °C, or 100 °C to 750 °C, or 150 °C to 750 °C, or 200 °C to 750 °C, or 250 °C to 750 °C, or 300 °C to 750 °C, or 350 °C to 750 °C, or 400 °C to 750 °C. In some aspects, the heat source can be an oven, a heat plate, a heated tube or other reaction vessel, an autoclave, or a combination thereof. In particular aspects, the temperature can range from 450 °C to 750 °C, such as 450 °C to 650 °C, or 450 °C to 600 °C, 450 °C to 575 °C, or 450 °C to 560 °C, or 450 °C to 555 °C, or 450 °C to 550 °C. In some aspects of the disclosure, the energy source can be used in combination with an inert gas (e.g., N₂ gas). In some aspects of the disclosure, the energy source can comprise a combination of UV light and heat. For example, in such aspects, the fluorine-containing compound can be exposed to the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) in the presence of UV light at a reaction temperature as described above. In some such aspects of the disclosure, the reaction temperature can range from a temperature greater than ambient temperature (e.g., above 25 °C) to a temperature of 400 °C, such as 50 °C to 350 °C, or 50 °C to 300 °C, or 50 °C to 250 °C, or 50 °C to 200 °C, or 50 °C to 150 °C.

[0059] In some aspects of the disclosure, the fluorine-containing compound and the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) are added to a reaction vessel (e.g., a reaction tube) used in the method simultaneously, substantially simultaneously, or sequentially to provide a reaction mixture. In some aspects of the disclosure, the fluorine-containing compound and the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) are added substantially simultaneously such that both components are added to a reaction vessel within a time period of less than 1 minute (e.g., less than 50 seconds, less than 40 seconds, less than 30 seconds, less than 20 seconds, or less than 10 seconds) relative to one another. In yet other aspects of the disclosure, the fluorine-containing compound and the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) are added sequentially, in any order. In some particular aspects, the fluorine-containing compound is added first, followed by the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂). In yet other particular aspects, halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) is added first, followed by the fluorine-containing compound.

[0060] In particular aspects of the disclosure, the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) used in the method starts in a liquid phase and is converted to a gas phase during the method and thus facilitates ease of handling when adding the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) to reaction vessels used in the method. In some aspects, the reaction vessel can be a reaction tube, which can be made of any suitable material as would be recognized by those in the art with the benefit of the present disclosure. In some aspects, the reaction tube can be made of a glass material (e.g., a borosilicate material or the like) or a metal material (e.g., a corrosion resistant metal material, such as an alloy). In particular aspects of the method, the reaction tube is a borosilicate material or an alloy (e.g., a nickel-based alloy, such as a Hastelloy alloy comprising nickel, chromium, and molybdenum).

[0061] The fluorine-containing compound and the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) can be added to the reaction vessel for a suitable time period and at a desired flow rate (e.g., liters per minute, or "LPM"). In some aspects of the disclosure, the fluorine-containing compound and the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂) can be added at the same or different flow rates. In some aspects of the disclosure, the flow rate of the fluorine-containing compound is slower than the flow rate of the halogen-based reagent (e.g., Br₂, IBr, ICl, BrCl, or Cl₂). In some exemplary aspects of the disclosure, a flow rate ratio ranging from 1:1 to 1:3 (Br₂:fluorine-containing compound) is used, such as a flow rate ratio of 1:2.5, or 1:1.7, or 1:1.3 (Br₂:fluorine-containing compound) is used. In yet additional aspects of the disclosure, a flow rate ratio ranging from 1:1 to 1:3 (Cl₂:fluorine-containing compound) is used, such as a flow rate ratio of 1:2.5, or 1:1.7, or 1:1.3 (Cl₂:fluorine-containing compound) is used. The flow rate is not necessarily limited and can be selected so as to control various aspects of the method, such as yield, compliance with safety protocols, and the like.

[0062] The halogen-based reagent and the fluorine-containing compound can be used in the method in amounts sufficient to give a molar ratio ranging from 10:1 to 1:10 (halogen-based reagent:fluorine-containing compound), such as 3.6:1 to 5.95:1, or 4:1 to 5.95:1, or 4.7:1 to 5.95:1, or 5.8:1 to 5.95:1. In exemplary aspects of the disclosure, the fluorine-containing compound and Br₂ are used in the method in amounts sufficient to give a molar ratio of 3.6:1, 4:1, 4.7:1, 5.8:1, or 5.95:1 (Br₂:fluorine-containing compound). In other exemplary aspects of the disclosure, the fluorine-containing compound and Cl₂ are used in the method in amounts sufficient to give a molar ratio of 3.6:1, 4:1, 4.7:1, 5.8:1, or 5.95:1 (Cl₂:fluorine-containing compound).

[0063] The method can further comprise condensing the reaction mixture formed from combining the fluorine-containing compound and the halogen-based reagent to thereby provide a liquid reaction product solution. In some aspects of the disclosure, condensing the reaction mixture can facilitate isolating desired product(s) from any remaining starting materials and/or any side-products. Condensing the reaction mixture can be accomplished by allowing the reaction mixture (which can comprise starting materials, side products, and/or desired product(s)) to flow through one or more condensing columns that are maintained at a temperature lower than the temperature at which the reaction vessel/tube is maintained. In some aspects of the disclosure, the temperature can be 0 °C or less, such as 0 °C to -50 °C, or 0 °C to -25 °C, or 0 °C to -10 °C. Upon cooling, the resulting liquid reaction product(s) can be isolated from the liquid reaction product solution in one or more reaction fractions. In some aspects of the disclosure, the one or more reaction fractions may comprise desired reaction products, side products, starting materials, or combinations thereof.

[0064] The method can further comprise one or more additional steps, such as performing one or more work-up procedures, separation procedures, and/or purification procedures. In some aspects of the present disclosure, the method can further comprise performing one or more work-up procedures wherein one or more reaction fractions is subjected to reagents suitable for quenching side products and/or starting materials. For example, HBr and/or HCl are side products produced in certain examples and residual Br₂, IBr, ICl, BrCl, or Cl₂ are starting materials that can be present in the reaction fraction(s). In some aspects of the disclosure, the work-up procedure comprises exposing the one or more reaction fractions to a basic solution (e.g., a solution comprising NaOH or the like) to neutralize any HBr present. In some additional aspects of the disclosure, the method can further comprise exposing the one or more reaction fractions to sodium thiosulfate pentahydrate and/or sodium metabisulfite to remove residual Br₂, IBr, ICl, BrCl, or Cl₂. The one or more reaction fractions can also be subjected to a separation procedure wherein an aqueous portion of any reaction fraction (e.g., such a reaction fraction that has been exposed to a work-up procedure) is removed from the organic (or fluorous) portion of the reaction fraction. In yet additional aspects of the disclosure, the method can further comprise a washing procedure

wherein any organic portion/fluorous portion is washed with H₂O. The desired reaction product can then be isolated from the washed mixture.

[0065] In some independent aspects of the disclosure, the method does not comprise using an autoclave. In such aspects, an autoclave is not used at any point during the method, nor in combination with any compounds of the method. In yet other independent aspects of the disclosure, the method does not comprise using activated carbon to facilitate the conversion of the fluorine-containing compound to the halogenated perfluoroaliphatic compound.

[0066] The method may further comprise converting the halogenated perfluoroaliphatic compound to a fluorotelomer, 1,3-hexafluorobutadiene (or "HFBD"), or the like. In some aspects of the disclosure, the method further comprises converting the halogenated perfluoroaliphatic compound to a fluorotelomer by reacting it with a fluorinated alkene compound, such as tetrafluoroethylene (or "TFE") in the presence of a promoter component, such as an energy source (e.g., light source, heat source, a radical initiator, or any combination thereof).

[0067] HFBD is a useful product in many industries. For example, HFBD is used as an etchant in the microelectronics industry. HFBD is considered environmentally friendly due to its low greenhouse warming potential (GWP = 0); thus, it is used in multiple etching processes, such as reactive ion etching (RIE), deep reactive ion etching (DRIE), plasma-enhanced chemical vapor deposition (PECVD) and chamber cleaning. Halogenated perfluoroaliphatic compounds according to the present disclosure can be readily converted to HFBD in one step. In some aspects of the disclosure, the halogenated perfluoroaliphatic compound is converted to HFBD by exposing the halogenated perfluoroaliphatic compound to magnesium-based compound, such as an aromatic magnesium halide compound (e.g., PhMgBr), an alkyl magnesium compound, including a monoalkyl magnesium halide or a dialkyl magnesium compound (or any complex, dimer, or polymer thereof), or an alkyl lithium compound. In some aspects, the monoalkyl magnesium halide is a monoalkyl magnesium halide compound (e.g., EtMgBr, BuMgBr, PrMgBr, EtMgCl, BuMgCl, or PrMgCl) and the dialkyl magnesium compound is a lower dialkyl magnesium species (e.g., (Me)₂Mg, (Et)₂Mg, (Bu)₂Mg, or the like). In representative aspects of the disclosure, the alkyl lithium compound comprises an alkyl group that has five or more carbon atoms, such as 6 or more carbon atoms. In particular representative aspects of the disclosure, the alkyl lithium compound is a hexyl lithium (e.g., *n*-hexyl lithium). In an independent aspect of the disclosure, the alkyl lithium compound is not, or is other than a butyl lithium, such as a butyl lithium selected from *n*-butyl lithium, *t*-butyl lithium, or *sec*-butyl lithium.

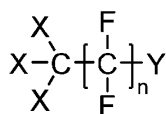
[0068] This one-step method with such reagents provides a substantial benefit relative to conventional methods used to make HFBD from fluorinated starting materials, which require multiple steps and/or undesirable reagents. Additionally, using an alkyl lithium compound

comprising an alkyl group having five or more carbon atoms, such as *n*-hexyl lithium, provides an advantage over alkyl lithium compounds comprising four carbon atoms (e.g., butyl lithium compounds). For example, using *n*-hexyl lithium avoids impurities that might be produced during the method (e.g., upon exposure to adventitious water that can be present) that can cause problems in isolating the HFBD, such as *n*-butane (which can be produced as a side product when using a butyl lithium compound). *n*-Butane has a boiling point of -1 °C, which is very similar to the boiling point of HFBD (5.5 °C) and thus complicates purification of the HFBD product. In contrast to butyl lithium compounds, *n*-hexyl lithium produces *n*-hexane upon reaction with water, which has a boiling point of 69 °C. Additionally, hexyl lithium is safer to handle and transport than butyl lithium compounds.

[0069] **Starting Materials and Products**

[0070] The method described herein can be used in combination with various different fluorine-containing compounds to provide different halogenated perfluoroaliphatic products comprising at least one halogen atom other than fluorine. The fluorine-containing compounds are linear (acyclic) compounds comprising at least two carbon-fluorine bonds and typically a plurality of carbon-fluorine bonds. In some particular aspects of the present disclosure, the fluorine-containing compound can be a linear acyclic compound comprising three or more fluorine atoms, with particular fluorine-containing compounds comprising four or more fluorine atoms. The fluorine-containing compound comprises at least one atom and/or functional group other than fluorine. Such atoms and/or functional groups can include hydrogen; a hydroxyl group; a carbonyl-containing group, such as a carboxylic acid group, an aldehyde group, an ester group, an anhydride group, or a ketone group; an amine group; a sulfonic acid group; a thiol group; an ether group, or any combinations thereof.

[0071] In some aspects of the disclosure, the fluorine-containing compound can have a structure according to Formula I



Formula I

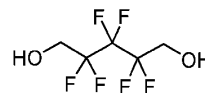
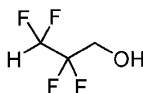
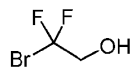
[0072] With reference to Formula I, each X independently is selected from H, F, Br, or -CH₂OH; n is an integer selected from 1 to 25, such as 1 to 22, or 1 to 20, or 1 to 18, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25; and Y is selected from H; -C(O)R or -[CH₂]_mOR (wherein R is hydrogen, aliphatic, cycloaliphatic, heteroaliphatic, cycloheteroaliphatic, haloaliphatic, cyclohaloaliphatic, aromatic, an organic functional group, or the

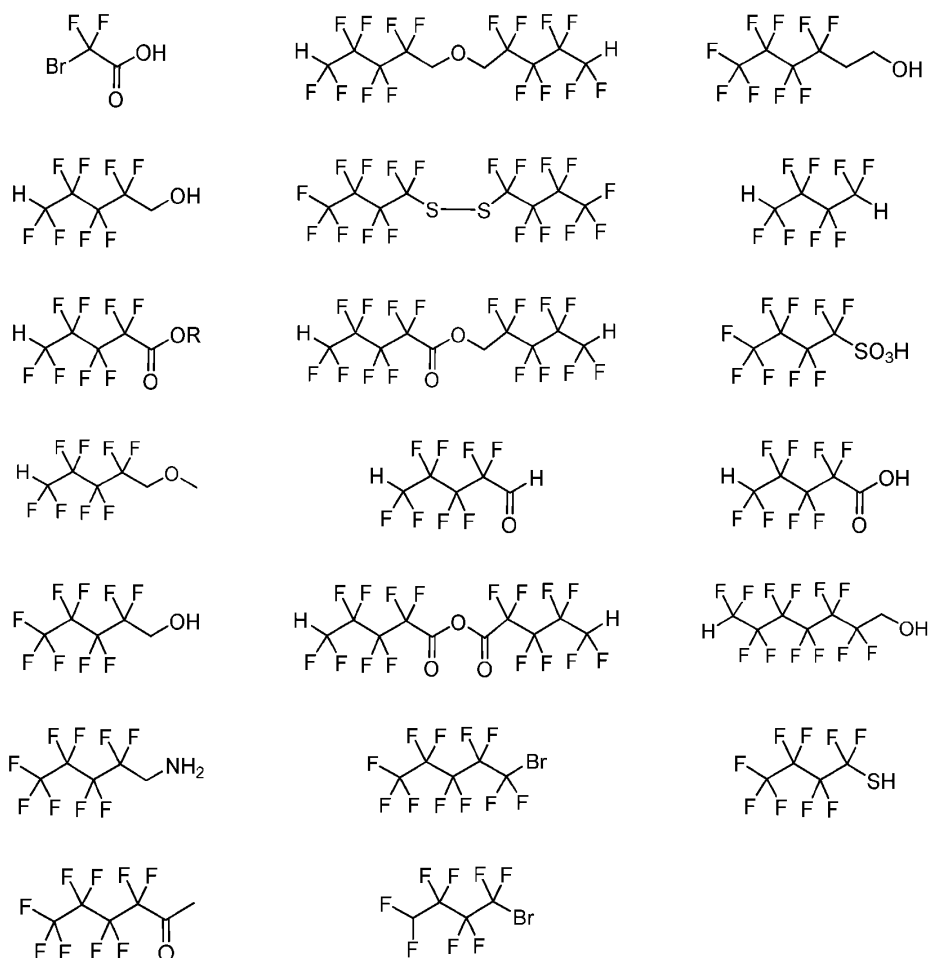
like; and m is an integer selected from 1 to 10, such as 1 to 8, or 1 to 6, or 1 to 4, or 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10); -C(O)OH; $-\text{[CH}_2\text{]}_m\text{NR}^a\text{R}^b$ (wherein each of R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, aromatic, cycloaliphatic, cycloheteroaliphatic, cyclohaloaliphatic, or an organic functional group and m is an integer selected from 1 to 10, such as 1 to 8, or 1 to 6, or 1 to 4, or 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10); $-\text{SO}_3\text{H}$; $-\text{SH}$; or $-\text{C(O)OR}'$, $-\text{C(O)OC(O)R}'$, $-\text{[CH}_2\text{]}_m\text{O[CH}_2\text{]}_m\text{R}'$, or $-\text{S-SR}'$ (wherein R' is aliphatic, cycloaliphatic, heteroaliphatic, cycloheteroaliphatic, aromatic, haloaliphatic, cyclohaloaliphatic, or the like; and m is an integer selected from 1 to 10, such as 1 to 8, or 1 to 6, or 1 to 4, or 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10). In an independent aspect of the disclosure, the fluorine-containing compound does not comprise an acyl fluoride group (i.e., $-\text{C(O)F}$).

[0073] In particular aspects of the disclosure, the R of the $-\text{C(O)R}$ or $-\text{[CH}_2\text{]}_m\text{OR}$ groups independently is selected from hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, or cycloalkynyl. In representative aspects of the disclosure, R is selected from hydrogen or lower alkyl (i.e., $\text{C}_1\text{-C}_{10}\text{alkyl}$). In particular aspects of the disclosure, each of R^a and R^b of the $-\text{[CH}_2\text{]}_m\text{NR}^a\text{R}^b$ group independently is selected from hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, cycloheteroalkyl, cycloheteroalkenyl, cycloheteroalkynyl, haloalkyl, haloalkenyl, haloalkynyl, cyclohaloalkyl, cyclohaloalkenyl, cyclohaloalkynyl, or an organic functional group as described herein. In representative aspects of the disclosure, each of R^a and R^b is H or lower alkyl (i.e., $\text{C}_1\text{-C}_{10}\text{alkyl}$). In particular aspects of the disclosure, the R' of the $-\text{C(O)OR}'$, $-\text{C(O)OC(O)R}'$, $-\text{[CH}_2\text{]}_m\text{O[CH}_2\text{]}_m\text{R}'$, or $-\text{S-SR}'$ groups can be selected from haloalkyl, haloalkenyl, haloalkynyl, cyclohaloalkyl, cyclohaloalkenyl, or cyclohaloalkynyl. In representative aspects of the disclosure, R' is a fluoroaliphatic group or a cyclofluoroaliphatic group, with particular aspects being $-\text{[(CF)}_2\text{]}_{1-5}\text{CF}_3$ or $-\text{[(CF)}_2\text{]}_{1-5}\text{CF}_2\text{H}$.

[0074] In particular aspects of the disclosure, Y is selected from H, $-\text{[CH}_2\text{]}_{1-10}\text{OH}$, $-\text{C(O)Me}$, $-\text{[CH}_2\text{]}_{1-10}\text{OMe}$, $-\text{C(O)OH}$, $-\text{C(O)H}$, $-\text{[CH}_2\text{]}_{1-10}\text{NH}_2$, $-\text{SO}_3\text{H}$, $-\text{SH}$, $-\text{C(O)O[CF}_2\text{]}_{1-10}\text{CF}_2\text{H}$, $-\text{C(O)OC(O)[CF}_2\text{]}_{1-10}\text{CF}_2\text{H}$, $-\text{[CH}_2\text{]}_m\text{O[CH}_2\text{]}_m\text{[CF}_2\text{]}_{1-10}\text{CF}_2\text{H}$, or $-\text{S-S[CF}_2\text{]}_{1-10}\text{CF}_2\text{H}$.

[0075] In particular aspects of the disclosure, the fluorine-containing compound can be selected from any of the following compounds.



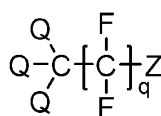


[0076] The fluorine-containing compounds according to the present disclosure can be obtained commercially or they can be made using methods known to those in the art with the benefit of the present disclosure.

[0077] The method described herein can be used to make myriad different halogenated perfluoroaliphatic compounds, particularly brominated and/or chlorinated products. In some aspects of the disclosure, the method can be used to make halogenated perfluoroaliphatic acyclic aliphatic compounds wherein the majority of carbon atoms of the compounds are bound to a fluorine atom with at least one carbon atom bound to a halogen selected from Br, Cl, or I. In particular aspects of the disclosure, the halogenated perfluoroaliphatic compounds made according to the disclosed method are brominated compounds that comprise at least one bromine atom. In some aspects of the disclosure, brominated perfluoroaliphatic compounds made according to the disclosed method comprise one or two bromine atoms. In yet other aspects of

the disclosure, chlorinated perfluoroaliphatic compounds comprising at least one chlorine atom can be made, including compounds comprising one or two chlorine atoms. Compounds made according to the disclosed method can comprise an acyclic linear or an acyclic branched carbon chain comprising one to 25 carbon atoms, such as 1 to 22, or 1 to 20, or 1 to 18, or 1 to 16, or 1 to 14, or 1 to 12, or 1 to 10, or 1 to 8, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25 carbon atoms.

[0078] In particular aspects of the present disclosure, the halogenated perfluoroaliphatic product has a structure according to Formula II, wherein each Q independently is Br, Cl, I, F, or H; Z is selected from Br, -CF₂Br, Cl, -CF₂Cl, I, or -CF₂I; and q is an integer selected from zero to 25, such as 1 to 22, or 1 to 20, or 1 to 18, or 1 to 16, or 1 to 14, or 1 to 12, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25.



Formula II

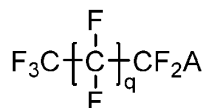
[0079] In particular aspects of the disclosure with respect to Formula II, each of the three Q groups can be F, or two of the Q groups can be F and the third Q group can be H or Br. In such aspects of the disclosure, Z is CF₂Br or CF₂Cl, preferably CF₂Br; and q is an integer ranging from zero to 25, such as zero to 8, or zero to 7, or zero to 6, or zero to 5, or zero to 4, or zero to 3, or zero to 2, or zero to 1. In some such aspects of the disclosure with respect to Formula II, each Q is F; Z is CF₂Br; and q is an integer selected from zero, 1, 2, 3, 4, 5, 6, 7, or 8. In yet other aspects of the disclosure with respect to Formula II, two Q groups are F; one Q group is H; Z is CF₂Br; and q is an integer selected from zero, 1, 2, 3, 4, 5, 6, 7, or 8.

[0080] In yet other aspects of the disclosure with respect to Formula II, one Q is Br, Cl, or H and the remaining two Q groups are F; Z is CF₂Br or CF₂Cl, preferably CF₂Br; and q is an integer ranging from zero to 25, such as zero to 8, or zero to 7, or zero to 6, or zero to 5, or zero to 4, or zero to 3, or zero to 2, or zero to 1. In some such aspects, one Q is Br and the remaining two Q groups are F; Z is CF₂Br; and q is an integer selected from zero, 1, 2, 3, 4, 5, 6, 7, or 8.

[0081] In yet other aspects of the disclosure with respect to Formula II, one Q is Br, Cl, or H and the remaining two Q groups are F; Z is Br or Cl, preferably Br; and q is zero.

[0082] In some aspects of the disclosure, the halogenated perfluoroaliphatic product has a structure according to Formula IIA, wherein A is a halogen other than F; and q is an integer

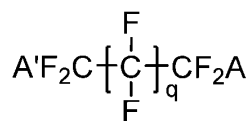
selected from zero to 25, such as 1 to 22, or 1 to 20, or 1 to 18, or 1 to 16, or 1 to 14, or 1 to 12, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25.



Formula IIA

[0083] In particular aspects of the disclosure with respect to Formula IIA, A is Br, Cl, or I; and q is an integer selected from zero to 8, or zero to 7, or zero to 6, or zero to 5, or zero to 4, or zero to 3, or zero to 2, or zero to 1. In some such aspects of the disclosure, A is Br or Cl, preferably Br; and q is an integer selected from zero, 1, 2, 3, 4, 5, 6, 7, or 8.

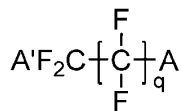
[0084] In some aspects of the disclosure, the halogenated perfluoroaliphatic product has a structure according to Formula IIB, wherein A is a halogen other than F; A' is F, Br, Cl, I, or H; and q is an integer selected from zero to 25, such as 1 to 22, or 1 to 20, or 1 to 18, or 1 to 16, or 1 to 14, or 1 to 12, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25.



Formula IIB

[0085] In particular aspects of the disclosure with respect to Formula IIB, A independently is selected from Br, Cl, or I; A' is F, Br, Cl, or H; and q is an integer selected from zero to 8, or zero to 7, or zero to 6, or zero to 5, or zero to 4, or zero to 3, or zero to 2, or zero to 1. In some such aspects of the disclosure, A is Br or Cl, preferably Br; A' is Br or H, preferably Br; and q is an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, or 8.

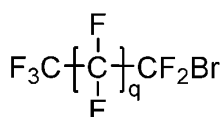
[0086] In some aspects of the disclosure, the halogenated perfluoroaliphatic product has a structure according to Formula IIC, wherein A is a halogen other than F; A' is F, Br, Cl, I, or H; and q is zero.



Formula IIC

[0087] In particular aspects of the disclosure with respect to Formula IIC, A is selected from Br, Cl, or I; A' is F, Br, Cl, or H; and q is zero. In some such aspects of the disclosure, A is Br or Cl, preferably Br; A' is Br or H, preferably Br; and q is zero.

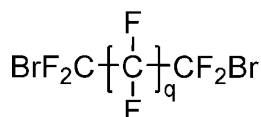
[0088] In some aspects of the disclosure, the halogenated perfluoroaliphatic product is a brominated perfluoroaliphatic product that has a structure according to Formula IIA', wherein q is an integer selected from zero to 25, such as 1 to 22, or 1 to 20, or 1 to 18, or 1 to 16, or 1 to 14, or 1 to 12, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25.



Formula IIA'

[0089] In particular aspects of the disclosure with respect to Formula IIA', q is an integer selected from zero to 8, or zero to 7, or zero to 6, or zero to 5, or zero to 4, or zero to 3, or zero to 2, or zero to 1. In some such aspects of the disclosure, q is an integer selected from zero, 1, 2, 3, 4, 5, 6, 7, or 8.

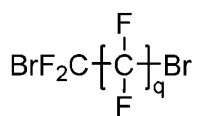
[0090] In some aspects of the disclosure, the brominated perfluoroaliphatic product has a structure according to Formula IIB', wherein q is an integer selected from zero to 25, such as 1 to 22, or 1 to 20, or 1 to 18, or 1 to 16, or 1 to 14, or 1 to 12, including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25.



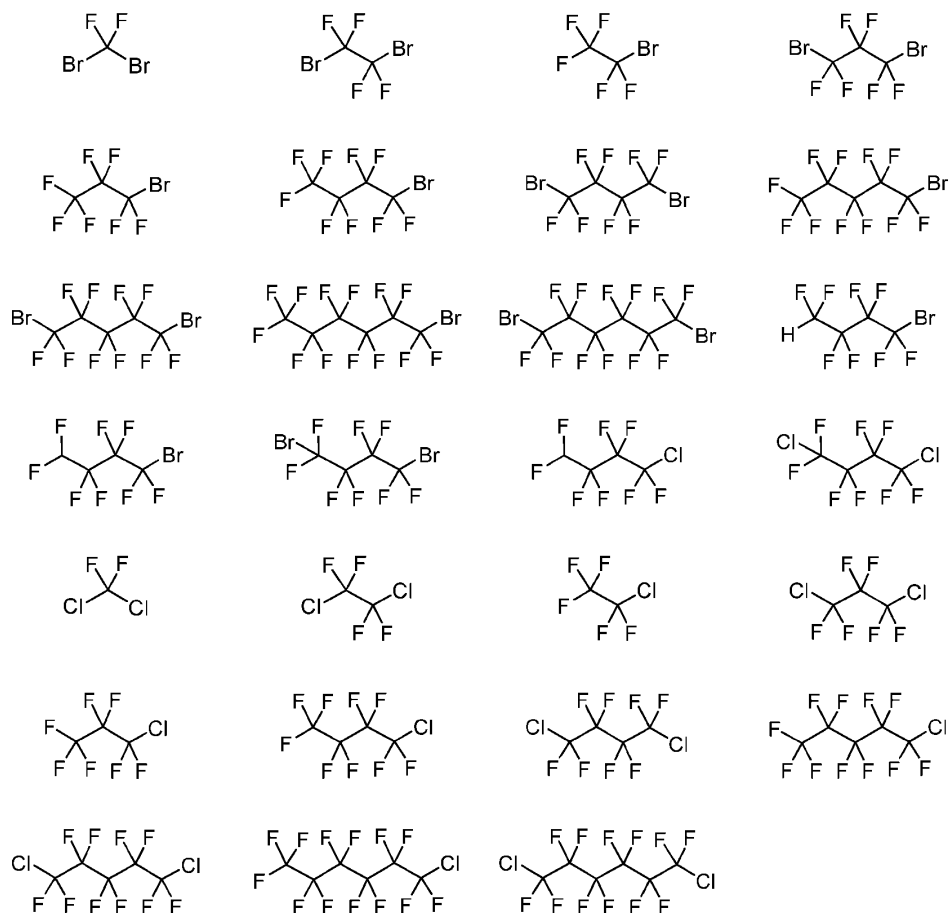
Formula IIB'

[0091] In particular aspects of the disclosure with respect to Formula IIB', q is an integer selected from zero to 8, or zero to 7, or zero to 6, or zero to 5, or zero to 4, or zero to 3, or zero to 2, or zero to 1. In some such aspects of the disclosure, q is an integer selected from zero, 1, 2, 3, 4, 5, 6, 7, or 8.

[0092] In some aspects of the disclosure, the brominated perfluoroaliphatic product has a structure according to Formula IIC', wherein q is zero.

**Formula IIC'**

[0093] In particular aspects of the disclosure, the method can be used to make any of the following halogenated perfluoroaliphatic products.

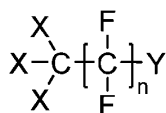


[0094] In some aspects of the disclosure, a mixture of halogenated perfluoroaliphatic products may be obtained; however, using the disclosed method provides the ability to selectively isolate more of a desired halogenated perfluoroaliphatic product over another. In some aspects of the disclosure, the method provides the ability to isolate a product mixture that favors a halogenated perfluoroaliphatic compound that comprises one terminal halogen atom (other than fluorine) over a halogenated perfluoroaliphatic compound that comprises two terminal halogen atoms (other than fluorine). Solely by way of example, the method disclosed herein can provide a product mixture of

1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (or “BOFB”) and 1,4-dibromooctafluorobutane (or “DBOFB”), wherein the BOFB is obtained with a higher selectivity than the DBOFB (e.g., a 9:1 ratio, BOFB:DBOFB can be obtained in some representative aspects). Such selectivity can be achieved with other products described herein using the disclosed method.

[0095] **Overview of Several Aspects**

[0096] Disclosed herein is a method for making a halogenated perfluoroaliphatic compound, comprising: exposing a fluorine-containing compound having a structure according to Formula I to a halogen-based reagent at a reaction temperature ranging from greater than ambient temperature to a temperature of 750 °C to provide a reaction mixture; and isolating the halogenated perfluoroaliphatic compound from the reaction mixture; wherein Formula I is



Formula I

wherein each X independently is selected from H, F, Br, or -CH₂OH; n is an integer selected from 1 to 25; and Y is selected from H, -C(O)OH, -SO₃H, -SH; or -C(O)R or -[CH₂]_mOR, wherein R is hydrogen, aliphatic, or cycloaliphatic, and m is an integer selected from 1 to 10; or -[CH₂]NR^aR^b, wherein each of R^a and R^b independently is selected from hydrogen, aliphatic, heteroaliphatic, haloaliphatic, aromatic, or an organic functional group; or -C(O)OR', C(O)OC(O)R', -[CH₂]_mO-[CH₂]_mR' or -S-SR', wherein R' is a haloaliphatic group and m is an integer selected from 1 to 10; provided that (i) if Y is -[CH₂]_mOR, wherein R is H and m is 1; (ii) n is 3; and (iii) two X groups are F and one X group is H, then the halogen-based reagent is not Cl₂.

[0097] In any or all of the above aspects, the reaction temperature ranges from 150 °C to 650 °C.

[0098] In any or all of the above aspects, the reaction temperature ranges from 450 °C to 600 °C.

[0099] In any or all of the above aspects, the method further comprises exposing the fluorine-containing compound, the halogen-based reagent, or both, to an inert gas.

[0100] In any or all of the above aspects, the inert gas is N₂ and the halogen-based reagent is Br₂, IBr, ICl, BrCl, or Cl₂.

[0101] In any or all of the above aspects, isolating the halogenated perfluoroaliphatic compound from the reaction mixture comprises condensing the reaction mixture to provide a liquid reaction product mixture.

[0102] In any or all of the above aspects, condensing the reaction mixture comprises passing the reaction mixture through one or more condensing columns.

[0103] In any or all of the above aspects, the halogenated perfluoroaliphatic compound is obtained in a reaction fraction obtained from passing the reaction mixture through the one or more condensing columns and wherein the reaction fraction is subjected to a work-up procedure, a separation procedure, a purification procedure, or any combination thereof.

[0104] In any or all of the above aspects, the method further comprising converting the halogenated perfluoroaliphatic compound to a fluorotelomer.

[0105] In any or all of the above aspects, the method further comprises converting the halogenated perfluoroaliphatic compound to 1,3-hexafluorobutadiene.

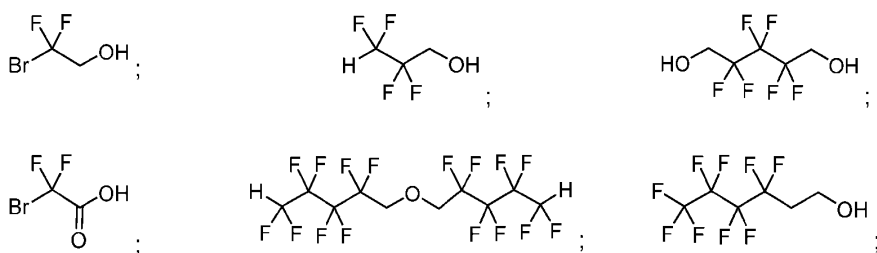
[0106] In any or all of the above aspects, R is selected from hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, or cycloalkynyl.

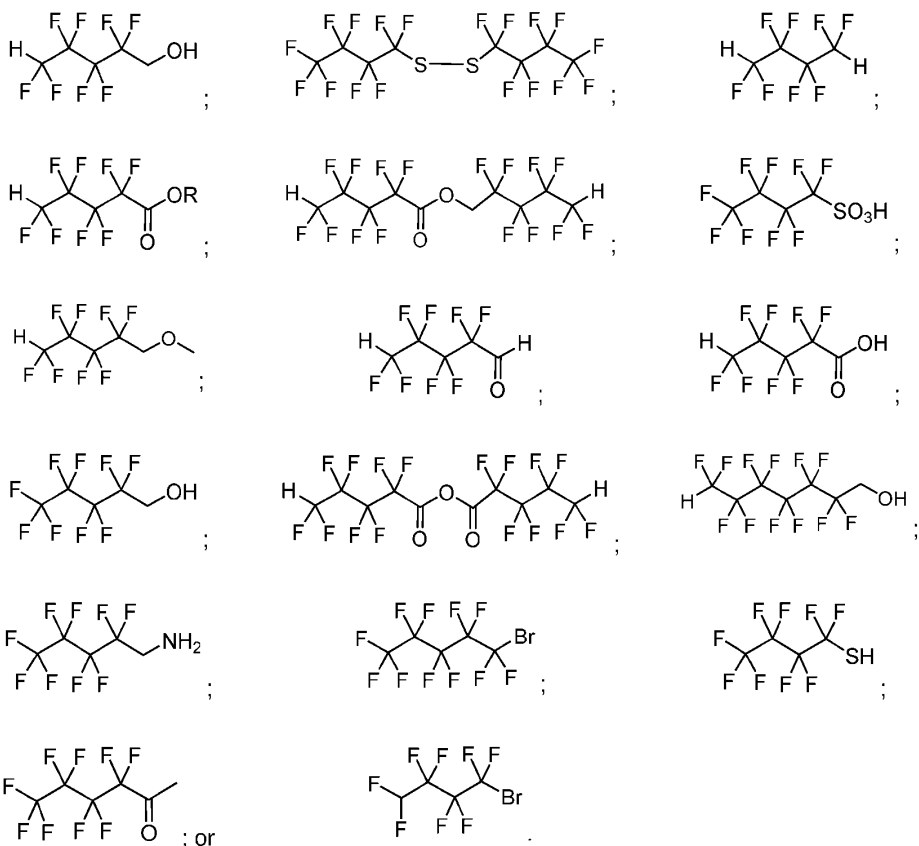
[0107] In any or all of the above aspects, each of R^a and R^b independently is selected from hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, cycloheteroalkyl, cycloheteroalkenyl, cycloheteroalkynyl, haloalkyl, haloalkenyl, haloalkynyl, cyclohaloalkyl, cyclohaloalkenyl, cyclohaloalkynyl, or an organic functional group.

[0108] In any or all of the above aspects, R¹ is selected from haloalkyl, haloalkenyl, haloalkynyl, cyclohaloalkyl, cyclohaloalkenyl, or cyclohaloalkynyl.

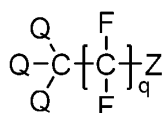
[0109] In any or all of the above aspects, Y is selected from H, -C(O)Me, -[CH₂]₁₋₁₀OH, -[CH₂]₁₋₁₀OMe, -C(O)OH, -C(O)H, -[CH₂]₁₋₁₀NH₂, -SO₃H, -SH, -C(O)O[CF₂]₁₋₁₀CF₂H, -C(O)OC(O)[CF₂]₁₋₁₀CF₂H, -[CH₂]_mO[CH₂]_m[CF₂]₁₋₁₀CF₂H, or -S-S[CF₂]₁₋₁₀CF₂H.

[0110] In any or all of the above aspects, the fluorine-containing compound is selected from





[0111] In any or all of the above aspects, the halogenated perfluoroaliphatic compound has a structure according to Formula II



Formula II

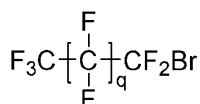
wherein each Q independently is Br, Cl, F, or H; Z is selected from Br, -CF₂Br, Cl, -CF₂Cl, I, or -CF₂I; and q is an integer selected from zero to 25; provided that the halogenated perfluoroaliphatic compound is not, or is other than, 1-chloro-1,1,2,2,3,3,4,4-octafluorobutane.

[0112] In any or all of the above aspects, each Q is F; Z is CF₂Br; and q is an integer ranging from zero to 18.

[0113] In any or all of the above aspects, one Q is Br or H and the remaining two Q groups are F; Z is CF₂Br; and q is an integer ranging from zero to 18.

[0114] In any or all of the above aspects, one Q is Br and the remaining two Q groups are F; Z is Br; and q is zero.

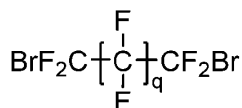
[0115] In any or all of the above aspects, the halogenated perfluoroaliphatic product has a structure according to Formula IIA'



Formula IIA'

wherein q is an integer selected from zero to 8.

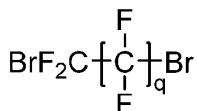
[0116] In any or all of the above aspects, the halogenated perfluoroaliphatic compound has a structure according to Formula IIB'



Formula IIB'

wherein q is an integer selected from zero to 8.

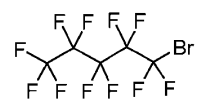
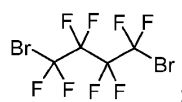
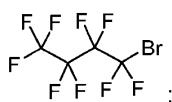
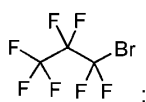
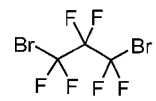
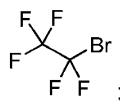
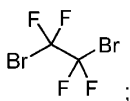
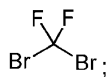
[0117] In any or all of the above aspects, the halogenated perfluoroaliphatic compound has a structure according to Formula IIC'

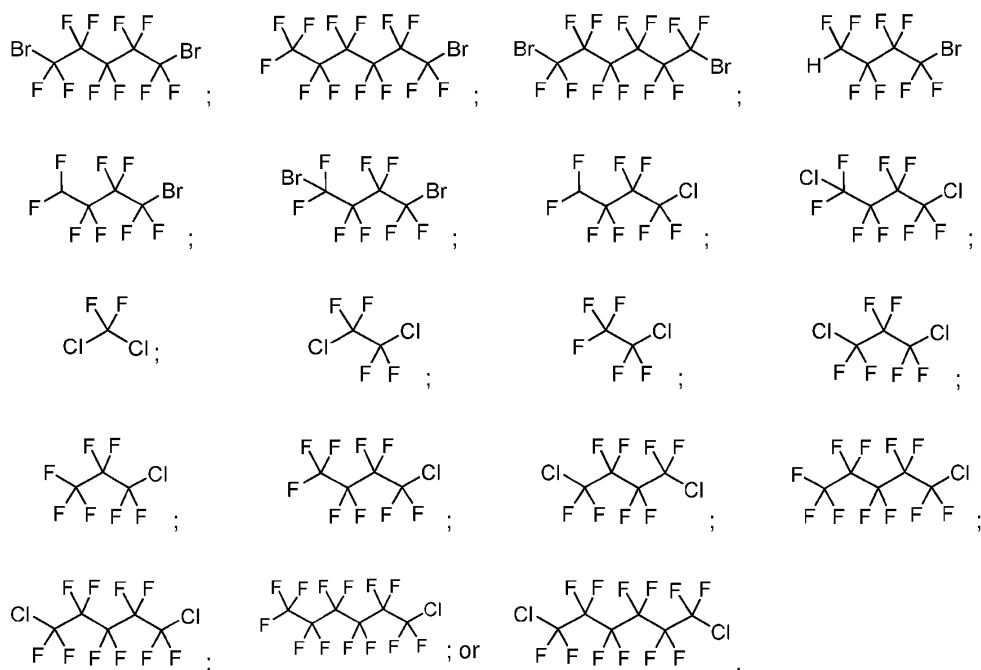


Formula IIC'

wherein q is zero.

[0118] In any or all of the above aspects, the halogenated perfluoroaliphatic compound is selected from





[0119] Also disclosed herein are aspects of a method for making 1,3-hexafluorobutadiene, comprising exposing 1,4-dibromo-1,1,2,2,3,3,4,4-octafluorobutane or 1,4-dichloro-1,1,2,2,3,3,4,4-octafluorobutane to an alkyl magnesium compound, an aromatic magnesium compound, or alkyl lithium compound comprising an alkyl group comprising five or more carbon atoms.

[0120] In any or all of the above aspects, the alkyl lithium compound is *n*-hexyl lithium; or the alkyl magnesium compound is EtMgBr, BuMgBr, PrMgBr, EtMgCl, BuMgCl, PrMgCl, (Me)₂Mg, (Et)₂Mg, or (Bu)₂Mg; or the aromatic magnesium compound is PhMgBr.

[0121] Also disclosed herein is a method for making a fluorotelomer, comprising reacting a halogenated perfluoroaliphatic compound made according to the disclosed method with a fluorinated alkene compound in the presence of a promoter component.

[0122] In any or all of the above aspects, the fluorinated alkene compound is tetrafluoroethylene and the promoter component is a light source, heat source, radical initiator, or a combination thereof.

[0123] **Examples****Example 1**

[0124] Synthesis of 1,4-dibromooctafluorobutane (DBOBF, CAS 335-48-8) - A vertically oriented borosilicate tube heated to 220 °C was connected via a 90° ball/socket elbow to a quartz tube (~30" heated length) placed horizontally in a tube furnace. To the pre-furnace portion of the big tube was added a layer of quartz cylinders roughly covering the bottom, and the pre-furnace portion of the big tube was heated to ~180 °C with two strands of heat tape. At the end of the furnace tube, a condensing system was attached with three, sequential condenser columns fitted to jacketed collection flasks. The first two condensing systems were set at 0 °C and the third condensing system included a collection flask maintained at -50 °C, with the condensers maintained at 0 °C. A final scrubbing system was set up after the third condenser system connected to a scrubbing column and bucket of aqueous sodium hydroxide and sodium thiosulfate before venting into the fume hood. With a constant N₂ flow of 1.5 L/min, the furnace portion of the big tube was heated to 550 °C for the simultaneous addition of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (OFPO, 305 g, 183 mL, 1.31 mol, 1 equiv.) via Hamilton dual syringe pump at 1.6 mL/min (27 µL/sec) and bromine (1000 g, 322.4 mL, 6.257 mol, 4.76 equiv.) via a bromine diaphragm pump at an effective rate of 2.7 mL/min into the vertical tube through 1/8" OD PTFE tubing. The lines were directed such that they would drip the reactants onto glass beads at the top of the tube. The reactants were added continuously for 2 hours at which point the addition of alcohol was stopped. The bromine flow was stopped ~1 minute later. The setup was then allowed to sit with only N₂ flowing for ~10 minutes. The reaction mixture was drained from the collection flasks. The contents of each flask were as follows: 1st collection flask = 425 g collected, analysis indicated 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (BOFB, 19.2% by mol fraction), 1,4-dibromooctafluorobutane (DBOBF, 75% by mol fraction) and 1,2-dibromotetrafluoroethane (DBTFE, 5.3% by mol fraction); 2nd collection flask = 375 g collected, analysis indicated BOFB (55.3%), DBOBF (39.8% by mol fraction) and DBTFE (4.8% by mol fraction); and 3rd collection flask = 53.4 g collected, analysis indicated BOFB (63.4% by mol fraction), DBOBF (30% by mol fraction) and DBTFE (6.6% by mol fraction). The 1st collection flask was subjected to workup to quench HBr and residual bromine by slow addition to cooled (0 °C) aq. NaOH (825 mL, 2.7 M) followed by the slow addition of solid sodium thiosulfate pentahydrate (70 g total) was slowly added to the cold mixture. The aqueous and fluorous layers were separated. The fluorous layer was washed with H₂O (2 x 150 mL) and the fluorous layer separated as a colorless liquid (230 g). Analysis indicated DBOBF (73% by moles, 78% by mass), BOFB (25% by moles, 21% by mass), and DBTFE (1.7% by moles, 1.3% by mass). Characterization Data of 1st Collection Flask: DBOBF (73%): ¹⁹F NMR (377 MHz, CDCl₃) δ -63.8 (t, J = 11.3 Hz, 4F), -116.7 (t, J = 11.3 Hz, 4F), see FIG. 1. BOFB (25%): ¹H NMR (400 MHz, CDCl₃) δ 6.0 (tt, J = 52.0, 5.1 Hz, 1H), see FIG. 2A.

^{19}F NMR (377 MHz, CDCl_3) δ -64.0 (t, J = 12.6 Hz, 2F), -119.1 (s, 2F), -128.8 (s, 2F), -137.3 (d, J = 52.6 Hz, 2F), see FIG. 2B. DBTFE (1.7%): ^{19}F NMR (377 MHz, CDCl_3) δ -63.2 (s, 4F), see FIG. 3. The 2nd and 3rd collection flasks were combined and processed similarly to yield a colorless liquid (115 g). Analysis indicated DBOFB (40% by moles, 43% by mass), BOFB (55% by moles, 46% by mass), and DBTFE (5.2% by moles, 4.0% by mass). Overall, the combined collection flasks (1-3) provided DBOFB (48% yield) and BOFB (27% yield). Characterization Data of combined 2nd and 3rd Collection Flasks: DBOFB (40%): ^{19}F NMR (377 MHz, CDCl_3) δ -63.7 (t, J = 11.4 Hz, 4F), -116.7 (t, J = 11.3 Hz, 4F); BOFB (55%): ^1H NMR (400 MHz, CDCl_3) δ 6.0 (tt, J = 52.0, 5.1 Hz, 1H); ^{19}F NMR (377 MHz, CDCl_3) δ -64.0 (t, J = 12.6 Hz, 2F), -119.1 (s, 2F), -128.7 (s, 2F), -137.5 (d, J = 51.7 Hz, 2F); DBTFE (5.2%): ^{19}F NMR (377 MHz, CDCl_3) δ -63.2 (s, 4F). Results shown in FIGS. 4A and 4B.

[0125] The products BOFB and DBOFB can be separated and purified by distillation. Purified BOFB: ^1H NMR (400 MHz, CDCl_3) δ 6.03 (tt, J = 51.9, 5.1 Hz, 1H). ^{19}F NMR (377 MHz, CDCl_3) δ -64.2 – -64.4 (m, 2F), -119.3 – -119.5 (m, 2F), -128.9 – -129.1 (m, 2F), -137.5 (d, J = 51.8 Hz, 2F). Purified DBOFB: ^{19}F NMR (377 MHz, CDCl_3) δ -64.1 (t, J = 11.4 Hz, 4F), -117.0 (t, J = 11.1 Hz, 4F).

Example 2

[0126] Synthesis of 1,4-dibromooctafluorobutane (DBOFB, CAS 335-48-8) - A vertically oriented borosilicate tube heated to 220 °C was connected via a 90° ball/socket elbow to a quartz tube (~30" heated length) placed horizontally in a tube furnace. To the pre-furnace portion of the big tube was added a layer of quartz cylinders roughly covering the bottom, and the pre-furnace portion of the big tube was heated to ~180 °C with two strands of heat tape. At the end of the furnace tube, a condensing system was attached with three, sequential condenser columns fitted to jacketed collection flasks. The first two condensing systems were set at 0 °C and the third condensing system included the collection flask set, which was maintained at -50 °C, with the condensers being maintained at 0 °C. A final scrubbing system was set up after the third condenser system connected to a scrubbing column and bucket of aqueous sodium hydroxide and sodium thiosulfate before venting into the fume hood. With a constant N_2 flow of 1.5 L/min, the furnace portion of the big tube was heated to 550 °C for the simultaneous addition of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (OFPO, 235 g, 137 mL, 1.16 mol, 1 equiv.) via Hamilton dual syringe pump at 1.8 mL/min (30 $\mu\text{L}/\text{sec}$) and bromine (Br_2 , 665 g, 214 mL, 4.16 mol, 3.58 equiv.) via a bromine diaphragm pump at effective rate of 2.4 mL/min into the vertical tube through 1/8" OD PTFE tubing. The lines were directed such that they would drip the reactants onto glass beads at the top of the tube. Once the lines were primed, the reactants were added continuously for 2 hours at which point the addition of OFPO was stopped. The bromine flow was stopped ~1 minute later. The reaction mixture was drained from the collection flasks. The contents of the collection

flasks were as follows: 1st collection flask = 351.5 g, analysis indicated 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (BOFB, 29% by mol fraction), 1,4-dibromooctafluorobutane (DBOFB, 66% by mol fraction), residual OFPO (2.9% by mol fraction), and 1,2-dibromotetrafluoroethane (DBTFE, 2.3% by mol fraction); 2nd collection flask = 225 g, analysis indicated BOFB (49% by mol fraction), DBOFB (28% by mol fraction), residual OFPO (19% by mol fraction) and DBTFE (4.5% by mol fraction); and 3rd collection flask = 36.422 g, analysis indicated BOFB (50% by mol fraction), DBOFB (18% by mol fraction), residual OFPO (24% by mol fraction), and DBTFE (6.9% by mol fraction). The collection flasks were combined. The combined crude material was subjected to workup to quench HBr and residual bromine by slow addition to cooled (0 °C) aq. NaOH (2.7 M) followed by the slow addition of solid sodium thiosulfate pentahydrate (120 g total) was slowly added to the cold mixture. The aqueous and fluoruous layers were separated. The fluoruous layer was washed with H₂O (2 x 250 mL) and fluoruous layer separated as a pale yellow liquid (302 g).

[0127] Analysis indicated DBOFB (59% by moles, 66% by mass), BOFB (34% by moles, 30% by mass), OFPO (4.0% by moles, 2% by mass), and DBTFE (2.9% by moles, 2% by mass). Overall, the combined collection flasks (1-3) provided DBOFB (47% yield). Characterization Data of combined Collection Flasks: DBOFB (59%): ¹⁹F NMR (377 MHz, CDCl₃) δ -64.1 (s, 4F), -117.0 (s, 4F). BOFB (34%): ¹H NMR (400 MHz, CDCl₃) δ 6.0 (tt, J = 51.9, 5.0 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -64.3 (s, 2F), -119.4 (s, 2F), -129 (s, 2F), -137.5 (d, J = 61.1 Hz). DBTFE (2.9%): ¹⁹F NMR (377 MHz, CDCl₃) δ -63.5 (s, 4F). Octafluorobutane (or "OFB") (4%): ¹H NMR (400 MHz, CDCl₃) δ 6.0 (tt, J = 51.9, 5.0 Hz, 2H). ¹⁹F NMR (377 MHz, CDCl₃) δ -131.3 (s, 4F), -137.8 (d, J = 52.9 Hz). Results shown in FIG. 5A and 5B

Example 3

[0128] Synthesis of 1,6-dibromodecafluorohexane (DBDFH, CAS 918-22-9) - A vertically oriented borosilicate tube heated to 220 °C was connected via a 90 ° ball/socket elbow to a quartz tube (~30" heated length) placed horizontally in a tube furnace. To the pre-furnace portion of the big tube was added a layer of quartz cylinders roughly covering the bottom, and the pre-furnace portion of the big tube was heated to ~180 °C with two strands of heat tape. At the end of the furnace tube, a condensing system was attached with three, sequential condenser columns fitted to jacketed collection flasks. The first two condensing systems were maintained at 0 °C and the third condensing system included the collection flask set, which was maintained -50 °C with the condensers maintained at 0 °C. A final scrubbing system was set up after the third condenser system connected to a scrubbing column and bucket of aqueous sodium hydroxide and sodium thiosulfate before venting into the fume hood. With a constant N₂ flow of 1.5 L/min, the furnace portion of the big tube was heated to 550 °C for the simultaneous addition of 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1-heptanol (DFHO, 360 g, 205 mL, 1.08 mol, 1 equiv.) via Hamilton dual syringe pump at 1.7 mL/min (29 µL/sec) and bromine (Br₂, 1030 g, 332.0 mL, 6.445

mol, 5.95 equiv.) via bromine diaphragm pump at effective rate of 2.8 mL/min into the vertical tube through 1/8" OD PTFE tubing. The lines were directed such that they would drip the reactants onto glass beads at the top of the tube. Once the lines were primed, the reactants were added continuously for 2 hours at which point the addition of DFHO was stopped. The bromine flow was stopped ~1 minute later. The reaction mixture was drained from the collection flasks. The collection flask contents were as follows: 1st collection flask = 630 g, analysis indicated primarily 1,6-dibromododecafluorohexane (DBDFH) along with 1-bromo-2,2,3,3,4,4,5,5,6,6-dodecafluorohexane (BDFH) and residual DFHO, but definitive ratios could not be determined due to significant signal overlap; 2nd collection flask = 330 g, analysis indicated primarily DBDFH along with BDFH and residual DFHO, but definitive ratios could not be determined due to significant signal overlap; and 3rd collection flask = 4.57 g, analysis indicated primarily DBDFH along with BDFH and residual DFHO, but definitive ratios could not be determined due to significant signal overlap. The 1st collection flask was subjected to workup to quench HBr and residual bromine by slow addition to cooled (0 °C) aq. NaOH (2.7 M) followed by the slow addition of solid sodium thiosulfate pentahydrate (130 g total) was slowly added to the cold mixture. The aqueous and fluorine layers were separated. The fluorine layer was washed with H₂O (1 x 165 mL, 1 x 80 mL) and fluorine layer separated as a colorless liquid (300 g).

[0129] Analysis indicated DBDFH (60% by moles, 64% by mass), BDFH (39% by moles, 35% by mass), and residual DFHO (1% by moles, 0.8% by mass). Characterization Data of 1st Collection Flask: DBDFH (60%): ¹⁹F NMR (377 MHz, CDCl₃) δ -64.1 (s, 4F), -117.8 (s, 4F), -121.2 – -122.1 (m, 4F). BDFH (39%): ¹H NMR (400 MHz, CDCl₃) δ 6.04 (tt, J = 52.0, 4.7 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -117.8 (s, 2F), -121.2 – -122.1 (m, 4F), -123.7 – -124.3 (m, 2F), -129.8 (s, 2F), -137.5 (d, J = 53.8 Hz, 2F). DFHO (1%): ¹H NMR (400 MHz, CDCl₃) δ 6.04 (tt, J = 52.0, 4.7 Hz, 1H), 4.10 (t, J = 13.7 Hz, 2H), [OH not observed]. ¹⁹F NMR (377 MHz, CDCl₃) δ -117.1 (s, 2F), -121.2 – -122.1 (m, 4F), -123.7 – -124.3 (m, 2F), -129.8 (s, 2F), -137.5 (d, J = 53.8 Hz, 2F). Results shown in FIGS. 6A and 6B.

[0130] The 2nd and 3rd collection flasks were combined and processed similarly to yield a colorless liquid (80 g). Analysis indicated DBDFH (53% by moles, 57% by mass), BDFH (45% by moles, 40 % by mass), and residual DFHO (2% by moles, 1.6% by mass). Overall, the combined collection flasks (1-3) provided DBDFH (48% yield) and BDFH (33% yield). Characterization Data of 2nd and 3rd Collection Flasks: DBDFH (53%): ¹⁹F NMR (377 MHz, CDCl₃) δ -63.7 – -64.4 (m, 4F), -117.5 – -118.0 (m, 4F), -121.3 – -121.7 (m, 4F). BDFH (45%): ¹H NMR (400 MHz, CDCl₃) δ 6.05 (tt, J = 51.9, 5.1 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -117.5 – -118.0 (m, 4F), -121.8 (s, 2F), -123.9 (s, 2F), -129.6 – -130.1 (m, 2F), -137.5 (dd, J = 52.0, 7.2 Hz, 2F). DFHO (2%): ¹H NMR (400 MHz, CDCl₃) δ 6.04 (td, J = 51.9, 5.1 Hz, 1H), 4.10 (td, J = 13.6, 7.3 Hz, 2H), 1.9 (t, J = 7.5

Hz, 1H). ^{19}F NMR (377 MHz, CDCl_3) δ -117.0 – -117.1 (m, 2F), -121.3 – -121.7 (m, 4F), -124.1 (s, 2F), -129.6 – -130.1 (m, 2F), -137.5 (dd, J = 52.0, 7.2 Hz, 2F). Results shown in FIGS. 7A and 7B.

Example 4

[0131] Synthesis of 1,2-dibromotetrafluoroethane (DBTFE, CAS 124-73-2). A vertically oriented borosilicate tube heated to 220 °C was connected via 90° ball/socket elbow to a quartz tube (~30" heated length) placed horizontally in a tube furnace. To the pre-furnace portion of the big tube was added a layer of quartz cylinders roughly covering the bottom, and the pre-furnace portion of the big tube was heated to ~180 °C with two strands of heat tape. At the end of the furnace tube, a condensing system was attached with a three, sequential condenser columns fitted to jacketed collection flasks. The first two condensing system was set at 0 °C and the third condensing system has the collection flask set at -50 °C and the condensers set at 0 °C. A final scrubbing system was set up after the third condenser system connected to a scrubbing column and bucket of aqueous sodium hydroxide and sodium thiosulfate before venting into the fume hood. With a constant N_2 flow of 1.5 L/min, the furnace portion of the big tube was heated to 550 °C for the simultaneous addition of 2,2,3,3-tetrafluoro-1-propanol (TFPO, 145 g, 98.0 mL, 1.10 mol, 1 equiv.) via Hamilton dual syringe pump at 0.81 mL/min (14 $\mu\text{L/s}$) and bromine (Br_2 , 1020 g, 328.8 mL, 5.81 Eq, 6.383 mol) via bromine diaphragm pump at effective rate of 2.7 mL/min into the vertical tube through 1/8" OD PTFE tubing. The lines were directed such that they would drip the reactants onto glass beads at the top of the tube. Once the lines were primed, the reactants were added continuously for 2 h at which point the addition of TFPO was stopped. The bromine flow was stopped ~1 min later. The reaction mixture was drained from the collection flasks. 1st collection flask: 260 g, analysis indicated primarily 1-bromo-1,1,2,2-tetrafluoroethane (BTFE, 6% by mol fraction) and 1,2-dibromotetrafluoroethane (DBTFE, 94% by mol fraction). 2nd collection flask: 225 g, analysis indicated BTFE (10% by mol fraction) and DBTFE (90% by mol fraction). 3rd collection flask: 36.422 g, analysis indicated BTFE (90% by mol fraction) and BDTFE (10% by mol fraction). The combined collection flasks were subjected to workup to quench HBr and residual bromine by slow addition to cooled (0 °C) aq. NaOH (2.7 M) followed by the slow addition of solid sodium thiosulfate pentahydrate (225 g total) was slowly added to the cold mixture. The aqueous and fluorous layers were separated. The fluorous layer was washed with H_2O (1 x 250 mL) and fluorous layer separated as a colorless liquid (98.06 g).

[0132] Analysis indicated primarily DBTFE (98% by moles, 99% by mass) and BTFE (2% by moles, 1% by mass). Overall, the combined collection flasks (1-3) provided DBTFE (34% yield) and BTFE (<1% yield). In some examples, the volatility of DBTFE and BTFE can contribute to reduced observed (isolated) yields. . Characterization Data of 1st Collection Flask: DBTFE (98%): ^{19}F NMR (377 MHz, CDCl_3) δ -63.5 (s, 4F). BTFE (2%): ^1H NMR (400 MHz, CDCl_3) δ 5.76 (tt, J =

53.7, 2.5 Hz, 1H). ^{19}F NMR (377 MHz, CDCl_3) δ -69.0 (t, J = 8.9 Hz, 2F), -131.1 (dt, J = 53.7, 9.1 Hz, 2F). Results shown in FIGS. 8A-8C.

Example 5

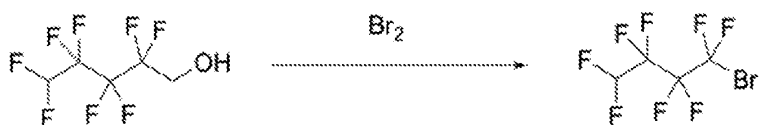
[0133] Synthesis of 1-Bromo-1,1,2,2,3,3,4,4-octafluorobutane (BOFB, CAS 558-86-1): quartz tube was placed horizontally in a tube furnace and the pre-furnace portion of the tube was separately heated to $\sim 180^\circ\text{C}$ with heat tape. At the end of the furnace tube, a condensing system was attached with two sequential 0°C condenser columns fitted to jacketed collection flasks. A final scrubbing system was set up after the second condenser system connected to a scrubbing column and bucket of aqueous sodium hydroxide and sodium thiosulfate before venting into the fume hood. With a constant N_2 flow of 1.5 L/min, the furnace portion of the big tube was heated to with increasing gradient in 3 zones (Zone 1: 400°C , Zone 2: 450°C , Zone 3: 500°C) for the simultaneous addition of 2,2,3,3,4,4,5,5-octafluoropentan-1-ol (OFPO, 60 g, 36 mL, 0.26 mol, 1 equiv.) via Hamilton dual syringe pump at 1.6 mL/min (27 $\mu\text{L}/\text{sec}$) and bromine (0.17 kg, 53 mL, 1.0 mol, 4 equiv.) via bromine diaphragm pump at 1.8 mL/min (108 mL/h), the latter delivered into hot tube via 1/4" OD PTFE tubing. The lines were directed such that they would drip the reactants onto the pre-furnace section of the tube. Once the lines were primed, the reactants were added continuously for 21 minutes at which point the addition of the alcohol was stopped followed by the bromine ~ 1 minute later. The collected reaction mixture was analyzed to contain residual OFPO (5.2%), 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (BOFB, 86%) and 1,4-dibromooctafluorobutane (DBOFB, 8.8%).

Example 6

[0134] Synthesis of Hexafluorobuta-1,3-diene (HFBD, CAS 685-63-2): To a flame dried, 3-neck flask equipped with magnetic stir bar, temperature probe, addition funnel and reflux condenser was added 1,4-dibromooctafluorobutane (DBOFB, 21.6 g, 10.3 mL, 60.0 mmol, 1 equiv.) and Et_2O (140 mL) under N_2 . The reflux condenser was connected with a canula to a flame dried, septum cap sealed 15 mL vial cooled to -78°C to condense released gases. This vessel was then connected through a needle to a N_2 Schlenk line with bubbler. The stirred solution was cooled to -78°C and as solution n -hexyllithium (52.2 mL, 120 mmol, 2.3 M in hexanes, 2 equiv.) was slowly added over 1 hour through the addition funnel at such a rate to keep the reaction temperature at or below -70°C . After an additional 45 minutes at -78°C , the cooling bath was removed and the reaction mixture was allowed to warm up. After 45 minutes, the reaction had reached 14°C . At this point, the reaction mixture was heated with a water bath set to 45°C . The first signs of distillate collection were observed when the pot reached 38°C . After heating 40 minutes, the bath temperature was increased to 50°C . After 1 hour, the bath was then removed and the pot was allowed to cool to room temperature. ^{19}F NMR using the standard trifluoromethoxybenzene that the additional HFBD was still present in the undistilled material. The sealed 15 mL vial was

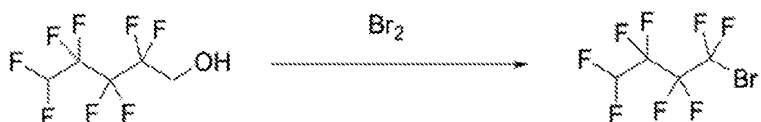
replaced (4.16 g collected) and the pot mixture was heated with the water bath set to 65-70 °C. After 45 minutes, the distillation was stopped and the distillation pot was allowed to cool to room temperature. The heating was immediately stopped, and the bath was removed. The sealed 15 mL vial was removed (1.155 g collected). ^{19}F NMR analysis of both collected fractions (5.3 g, 55% yield) indicated high purity of 1,3-hexafluorobutadiene (HFBD). HFBD: ^{19}F NMR (377 MHz, CDCl_3) δ -92.7 – -93.0 (m, 2F), -107.0 – -107.7 (m, 2F), -179.6 – -180.2 (m, 2F). See FIG. 9. GC-MS (EI) calcd. for C_4F_6^+ (M^+) 161.9899, found 162.1000. Note: A small amount of the solvent Et_2O was observed by ^1H NMR and GC-MS analysis.

Example 7



[0135] To a boiler column maintained at 140 °C, Bromine (6.455 kg, 40.4 mol) was charged over 255 minutes. The bromine vaporized and flowed through heat traced lines at 150 °C to a tube furnace where 1,1,2,2,3,3,4,4-octafluoro-1-pentanol (3.2 kg, 13.8 mol) was charged in parallel to a bed of quartz cylinders at the front the tube furnace maintained at 500 °C. The resulting effluent gas exited the tube furnace and was precooled via an Allihn condenser maintained at 80 °C. The resulting cooled effluent gas was treated in-line with a cooled aqueous sodium hydroxide and sodium metabisulfite quench solution, maintaining a quench solution temperature at approximately 40 °C. The treated gas stream flowed through two sets of pilot plant condensers set at 2 °C followed by two sets of pilot plant condensers set at -30 °C and a dry ice trap maintained at -78 °C. Once the charge was completed, the system was purged with clean nitrogen over 15 minutes. From the system, 3.520 kg of crude material was collected with the following approximate composition using GC-MS: 0.01% Dibromodifluoromethane, 6.93% 1,1,2,2,3,3,4,4-octafluorobutane, 0.24% 1,2-dibromotetrafluoroethane, 76.26% 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane, 16.56% 1,4-dibromooctafluorobutane.

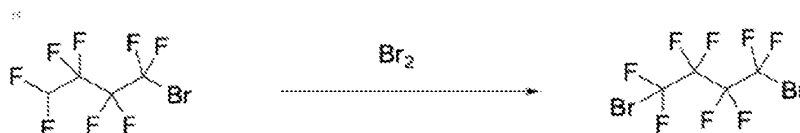
Example 8



[0136] To a Hastelloy c276 alloy tube maintained at 150 °C, Bromine (990g, 6.19 mol) was charged over 30 minutes with 1 LPM of clean Nitrogen. In parallel, 1,1,2,2,3,3,4,4-octafluoro-1-

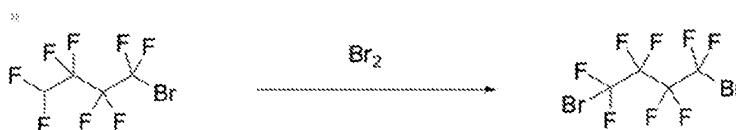
pentanol (290 g, 1.25 mol) was charged in parallel to a Hastelloy c276 tube maintained at 150 °C alongside 1 LPM of clean Nitrogen over 30 minutes. The two feeds passed through a tube furnace maintained at 550 °C. The feeds met, mixed and passed through a Hastelloy c276 tube reactor inside the tube furnace at 550 °C. The resulting effluent gas exited the tube furnace and was treated in-line with a cooled aqueous sodium hydroxide and sodium metabisulfite quench solution, maintaining a quench solution temperature at approximately 40 °C. The treated gas stream flowed through two sets of pilot plant condensers set at 2 °C followed by two sets of pilot plant condensers set at -30 °C and a dry ice trap maintained at -78 °C. Once the charge was completed, the system was purged with clean nitrogen over 20 minutes. From the system, 260 g crude material was collected with the following approximate composition using GC-MS: 0.05% Dibromodifluoromethane, 1.84% 1,1,2,2,3,3,4,4-octafluorobutane, 0.57% 1,2-dibromotetrafluoroethane, 78.21% 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane, and 19.14% 1,4-dibromooctafluorobutane.

Example 9



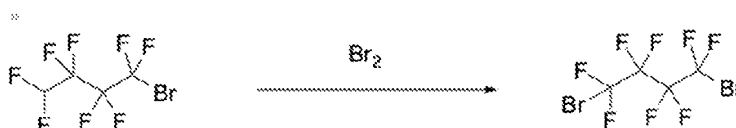
[0137] To a boiler column maintained at 140 °C, bromine (565 g, 3.54 mol) was charged over 70 minutes with a flow of Nitrogen gas at 2 LPM. The bromine vaporized and flowed through heat traced lines at 150 °C to a tube furnace where purified 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (660 g, 2.35 mol) was charged in parallel to a bed of quartz cylinders at the front the tube furnace maintained at 550 °C. The resulting effluent gas exited the tube furnace and was precooled via an Allihn condenser maintained at 80 °C. The resulting cooled effluent gas was treated in-line with a cooled aqueous sodium hydroxide and sodium metabisulfite quench solution, maintaining a quench solution temperature at approximately 30 °C. The treated gas stream flowed through two sets of pilot plant condensers set at 2 °C followed by two sets of pilot plant condensers set at -30 °C and a dry ice trap maintained at -78 °C. Once the charge was completed, the system was purged with clean Nitrogen over 15 minutes. From the system, crude material (520 g) was collected with the following approximate composition using GC-MS: 0.03% Tribromomethane (Bromoform), 0.31% 1,1,2,2,3,3,4,4-octafluorobutane, 0.92% 1,2-dibromotetrafluoroethane, 26.02% 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane, 72.62% 1,4-dibromooctafluorobutane, 0.1% Unknown impurity.

Example 10



[0138] To a boiler column maintained at 140 °C, Bromine (2.6 kg, 16.3 mol) was charged over 110 minutes. The bromine vaporized and flowed through heat traced lines at 150 °C to a tube furnace where crude 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (3.260 kg, 11.6 mol) was charged in parallel to a bed of quartz cylinders at the front the tube furnace maintained at 575 °C. The resulting effluent gas exited the tube furnace and was precooled via an Allihn condenser maintained at 80 °C. The resulting cooled effluent gas was treated in-line with a cooled aqueous sodium hydroxide and sodium metabisulfite quench solution, maintaining a quench solution temperature at approximately 40 °C. The treated gas stream flowed through two sets of pilot plant condensers set at 2 °C followed by two sets of pilot plant condensers set at -30 °C and a dry ice trap maintained at -78 °C. Once the charge was completed, the system was purged with clean Nitrogen over 15 minutes. From the system, crude material (3.630 kg) was collected with the following approximate composition using GC-MS: 0.01% Tribromomethane (Bromoform), 0.04% 1-bromo-1,1,2,2-tetrafluoroethane, 0.02% Dibromodifluoromethane, 0.70% 1,1,2,2,3,3,4,4-octafluorobutane, 1.77% 1,2-dibromotetrafluoroethane, 19.05% 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane, 78.42% 1,4-dibromooctafluorobutane.

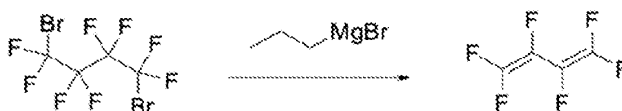
Example 11



[0139] To a Hastelloy c276 alloy tube maintained at 150 °C, Bromine (660g, 4.13 mol) was charged over 24 minutes. In parallel, crude 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane (730g, 2.61 mol) was charged in parallel to a Hastelloy c276 tube maintained at 150 °C. The two feeds passed through a tube furnace maintained at 575 °C. The feeds met, mixed and passed through a Hastelloy c276 tube reactor inside the tube furnace at 575 °C. The resulting effluent gas exited the tube furnace and was treated in-line with a cooled aqueous sodium hydroxide and sodium metabisulfite quench solution, maintaining a quench solution temperature at approximately 35 °C. The treated gas stream flowed through two sets of pilot plant condensers set at 2 °C followed by two sets of pilot plant condensers set at -30 °C and a dry ice trap maintained at -78 °C. Once the charge was completed, the system was purged with clean nitrogen over 10 minutes. From the system, 620 g crude material was collected with the following approximate composition using GC-

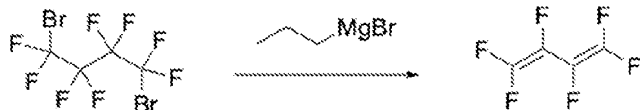
MS: 0.03% Dibromodifluoromethane, 0.34% 1,1,2,2,3,3,4,4-octafluorobutane, 1.07% 1,2-dibromotetrafluoroethane, 17.41% 1-bromo-1,1,2,2,3,3,4,4-octafluorobutane, 80.82% 1,4-dibromooctafluorobutane and 0.27% 1,3-dibromohexafluoropropane.

Example 12



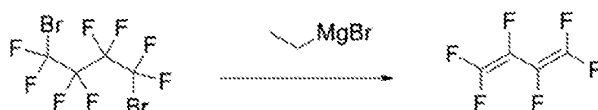
[0140] A solution of dibromooctafluorobutane (DBOFB, 210 g, 100 mL, 0.583 mol) in THF (200 mL) was prepared. A solution of propylmagnesium bromide (n-PrMgBr, 1.58 L, 2.7 equiv, 1M in THF) was pumped in a stainless steel pipe (3/16 in ID) at a rate of 790 $\mu\text{L}/\text{sec}$ into a static mixer where it meets the DBOFB/THF solution being pumped at a rate of 150 $\mu\text{L}/\text{sec}$ in a bath temperature of 20 $^{\circ}\text{C}$ through 12 ft of stainless steel tubing into a receiver flask cooled to 0 $^{\circ}\text{C}$. The crude solution was held at 0 $^{\circ}\text{C}$ for 1 hour prior to transfer to a container for storage and analysis. ^{19}F NMR analysis of the crude reaction mixture shows conversion of the DBOFB to hexafluorobutadiene (HFBD) as the major product (>80% by ^{19}F NMR).

Example 13



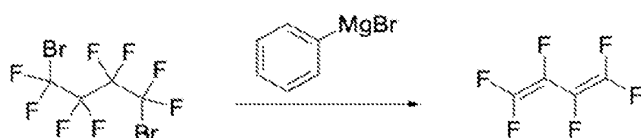
[0141] A solution of propylmagnesium bromide (n-PrMgBr, 700 mL, 2.4 equiv, 1M in THF) was pumped in a stainless steel pipe (3/16 in ID) at a rate of 1.400 mL/sec into a static mixer where it meets neat DBOFB (50 mL, 105 g, 0.292 mol) being pumped at a rate of 100 $\mu\text{L}/\text{sec}$ in a bath temperature of 15 $^{\circ}\text{C}$ through 12 ft of stainless steel tubing into a receiver flask cooled to 0 $^{\circ}\text{C}$. The crude solution was held at 0 $^{\circ}\text{C}$ for 1 hour prior to transfer to a container for storage and analysis. ^{19}F NMR analysis of the crude reaction mixture shows conversion of the DBOFB to hexafluorobutadiene (HFBD) as the major product (>80% by ^{19}F NMR).

Example 14



[0142] A solution of ethylmagnesium bromide (EtMgBr, 950 mL, 2.6 equiv, 0.85M in THF) was pumped in a stainless steel pipe (3/16 in ID) at a rate of 2.650 mL/sec into a static mixer where it meets neat DBOFB (155 g, 0.43 mol) being pumped at a rate of 150 μ L/sec in a bath temperature of 35 °C through 36 ft of stainless steel tubing into a receiver flask cooled to 0 °C. The crude solution was held at 0 °C for 1 hour prior to transfer to a container for storage and analysis. Distillation of the crude material gave hexafluorobutadiene (HFBD, 24 g, 34%) which was determined to be >80% pure by GC and ^{19}F NMR.

Example 15

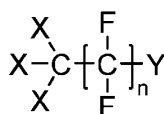


[0143] A solution of phenylmagnesium bromide (PhMgBr, 1000 mL, 2.6 equiv, 1.4 M in THF) was pumped in a stainless steel pipe (3/16 in ID) at a rate of 1.11 mL/sec into a static mixer where it meets neat DBOFB (195 g, 0.542 mol) being pumped at a rate of 100 μ L/sec in a bath temperature of 35 °C through 36 ft of stainless steel tubing into a receiver flask cooled to 0 °C. The crude solution was held at 0 °C for 1 hour prior to transfer to a container for storage and analysis. Distillation of the crude material gave hexafluorobutadiene (HFBD, 36 g, 41%) which was determined to be >80% pure by GC and ^{19}F NMR.

[0144] In view of the many possible aspects to which the principles of the present disclosure may be applied, it should be recognized that the illustrated aspects are only preferred examples of the disclosure and should not be taken as limiting the scope of the present disclosure. Rather, the scope of is defined by the following claims. We therefore claim as our invention all that comes within the scope and spirit of these claims.

We claim:

1. A method for making a halogenated perfluoroaliphatic compound, comprising:
 exposing a fluorine-containing compound having a structure according to Formula I to a
 halogen-based reagent at a reaction temperature ranging from greater than ambient temperature
 to a temperature of 750 °C to provide a reaction mixture; and
 isolating the halogenated perfluoroaliphatic compound from the reaction mixture; wherein
 Formula I is

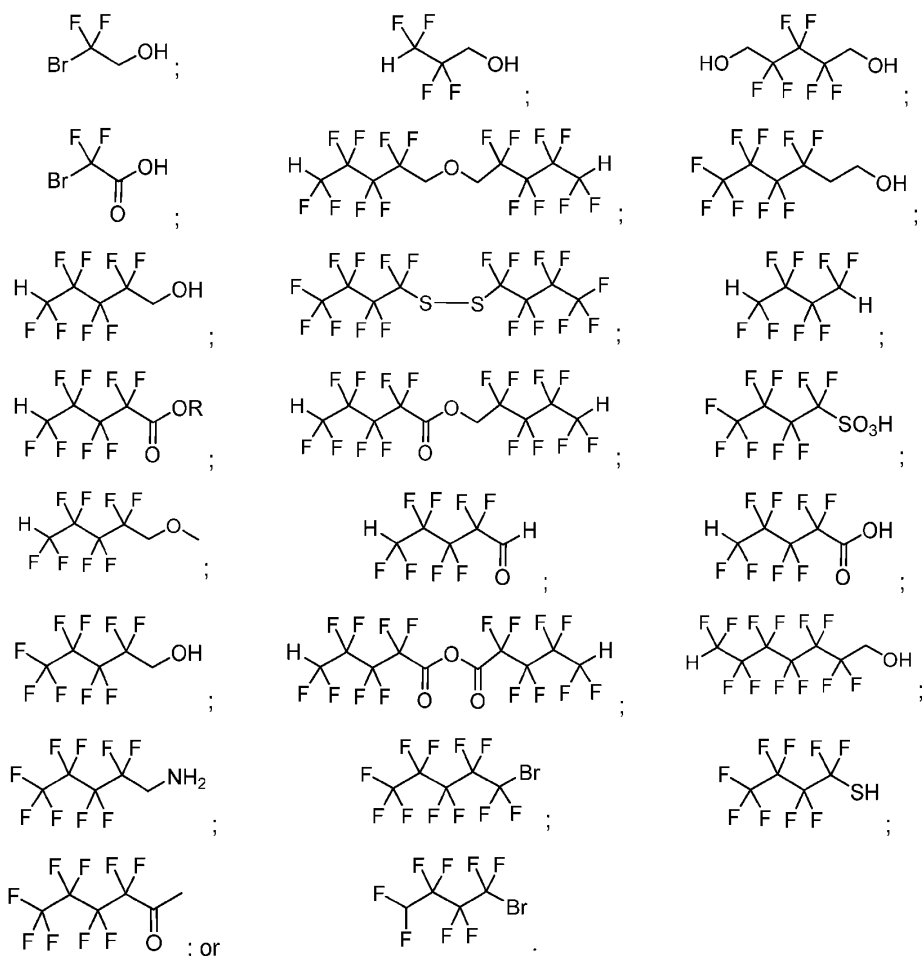


Formula I

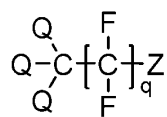
wherein

- each X independently is selected from H, F, Br, or -CH₂OH;
n is an integer selected from 1 to 25; and
Y is selected from
H, -C(O)OH, -SO₃H, -SH; or
-C(O)R or -[CH₂]_mOR, wherein R is hydrogen, aliphatic, or cycloaliphatic, and m is
an integer selected from 1 to 10; or
-[CH₂]NR^aR^b, wherein each of R^a and R^b independently is selected from hydrogen,
aliphatic, heteroaliphatic, haloaliphatic, aromatic, or an organic functional group; or
-C(O)OR', C(O)OC(O)R', -[CH₂]_mO-[CH₂]_mR' or -S-SR', wherein R' is a haloaliphatic
group and m is an integer selected from 1 to 10; provided that (i) if Y is -[CH₂]_mOR, wherein
R is H and m is 1; (ii) n is 3; and (iii) two X groups are F and one X group is H, then the
halogen-based reagent is not Cl₂.
2. The method of claim 1, wherein the reaction temperature ranges from 150 °C to
650 °C.
3. The method of claim 1, wherein the reaction temperature ranges from 450 °C to
600 °C.
4. The method of any one of claims 1-3, further comprising exposing the fluorine-
containing compound, the halogen-based reagent, or both, to an inert gas.
5. The method of claim 4, wherein the inert gas is N₂ and the halogen-based reagent
is Br₂, IBr, ICl, BrCl, or Cl₂.

6. The method of any one of claims 1-5, wherein isolating the halogenated perfluoroaliphatic compound from the reaction mixture comprises condensing the reaction mixture to provide a liquid reaction product mixture.
7. The method of claim 6, wherein condensing the reaction mixture comprises passing the reaction mixture through one or more condensing columns.
8. The method of claim 7, wherein the halogenated perfluoroaliphatic compound is obtained in a reaction fraction obtained from passing the reaction mixture through the one or more condensing columns and wherein the reaction fraction is subjected to a work-up procedure, a separation procedure, a purification procedure, or any combination thereof.
9. The method of any one of claims 1-9, wherein the method further comprising converting the halogenated perfluoroaliphatic compound to a fluorotelomer.
10. The method of any one of claims 1-9, wherein the method further comprises converting the halogenated perfluoroaliphatic compound to 1,3-hexafluorobutadiene.
11. The method of any one of claims 1-10, wherein R is selected from hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, or cycloalkynyl.
12. The method of any one of claims 1-10, wherein each of R^a and R^b independently is selected from hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, cycloheteroalkyl, cycloheteroalkenyl, cycloheteroalkynyl, haloalkyl, haloalkenyl, haloalkynyl, cyclohaloalkyl, cyclohaloalkenyl, cyclohaloalkynyl, or an organic functional group.
13. The method of any one of claims 1-10, wherein R' is selected from haloalkyl, haloalkenyl, haloalkynyl, cyclohaloalkyl, cyclohaloalkenyl, or cyclohaloalkynyl.
14. The method of any one of claims 1-10, wherein Y is selected from H, -C(O)Me, -[CH₂]₁₋₁₀OH, -[CH₂]₁₋₁₀OMe, -C(O)OH, -C(O)H, -[CH₂]₁₋₁₀NH₂, -SO₃H, -SH, -C(O)O[CF₂]₁₋₁₀CF₂H, -C(O)OC(O)[CF₂]₁₋₁₀CF₂H, -[CH₂]_mO[CH₂]_m[CF₂]₁₋₁₀CF₂H, or -S-S[CF₂]₁₋₁₀CF₂H.
15. The method of any one of claims 1-10, wherein the fluorine-containing compound is selected from



16. The method according to any one of claims 1-15, wherein the halogenated perfluoroaliphatic compound has a structure according to Formula II



Formula II

wherein

each Q independently is Br, Cl, F, or H;

Z is selected from Br, $-\text{CF}_2\text{Br}$, Cl, $-\text{CF}_2\text{Cl}$, I, or $-\text{CF}_2\text{I}$; and

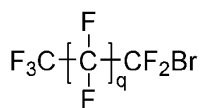
q is an integer selected from zero to 25; provided that the halogenated perfluoroaliphatic compound is not, or is other than, 1-chloro-1,1,2,2,3,3,4,4-octafluorobutane.

17. The method of any one of claims 1-16, wherein each Q is F; Z is CF₂Br; and q is an integer ranging from zero to 18.

18. The method of any one of claims 1-16, wherein one Q is Br or H and the remaining two Q groups are F; Z is CF₂Br; and q is an integer ranging from zero to 18.

19. The method of any one of claims 1-16, wherein one Q is Br and the remaining two Q groups are F; Z is Br; and q is zero.

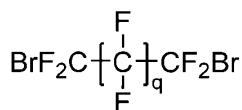
20. The method of any one of claims 1-16, wherein the halogenated perfluoroaliphatic product has a structure according to Formula IIA'



Formula IIA'

wherein q is an integer selected from zero to 8.

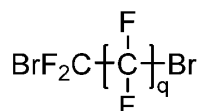
21. The method of any one of claims 1-16, wherein the halogenated perfluoroaliphatic compound has a structure according to Formula IIB'



Formula IIB'

wherein q is an integer selected from zero to 8.

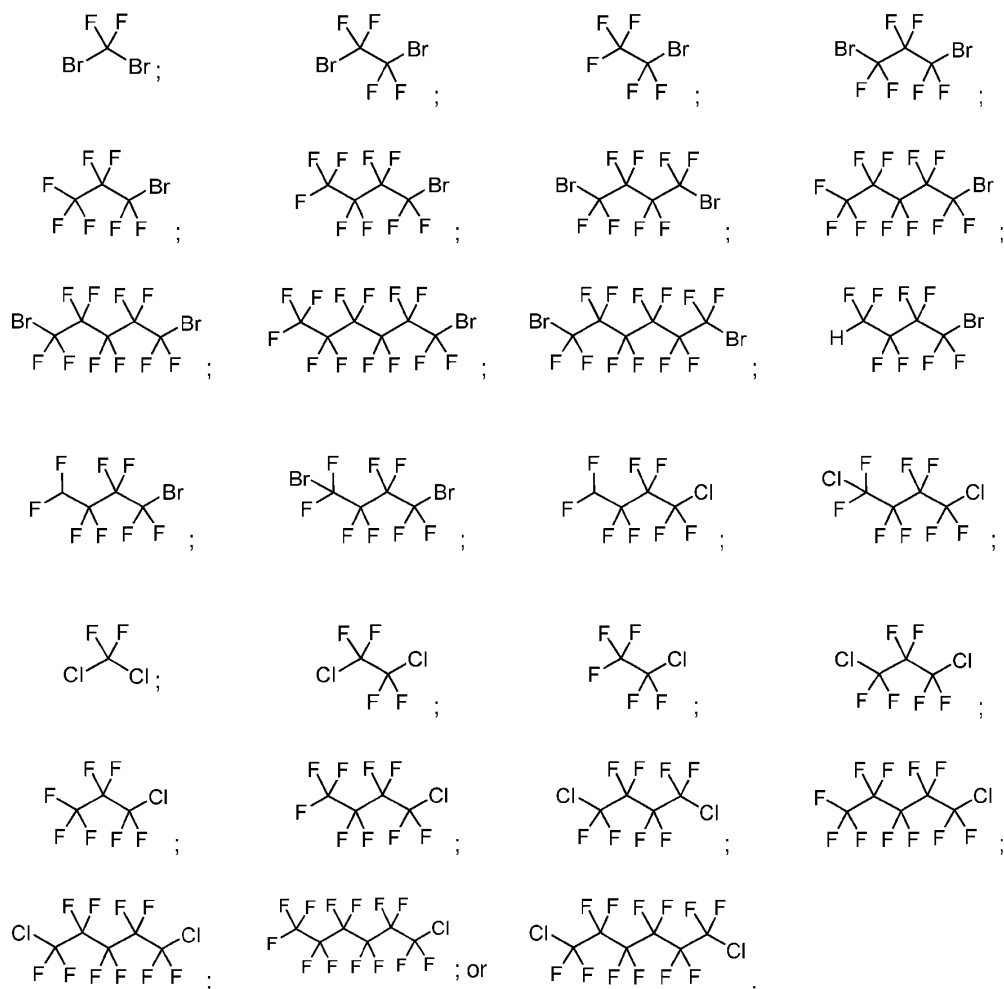
22. The method of any one of claims 1-16, wherein the halogenated perfluoroaliphatic compound has a structure according to Formula IIC'



Formula IIC'

wherein q is zero.

23. The method of any one of claims 1-16, wherein the halogenated perfluoroaliphatic compound is selected from



24. A method for making 1,3-hexafluorobutadiene, comprising exposing 1,4-dibromo-1,1,2,2,3,3,4,4-octafluorobutane or 1,4-dichloro-1,1,2,2,3,3,4,4-octafluorobutane to an alkyl magnesium compound, an aromatic magnesium compound, or alkyl lithium compound comprising an alkyl group comprising five or more carbon atoms.

25. The method of claim 24, wherein the alkyl lithium compound is *n*-hexyl lithium; or the alkyl magnesium compound is EtMgBr, BuMgBr, PrMgBr, EtMgCl, BuMgCl, PrMgCl, (Me)₂Mg, (Et)₂Mg, or (Bu)₂Mg; or the aromatic magnesium compound is PhMgBr.