

**(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE**

(11) Application No. AU 2008334034 B2

(54) Title
Sulfur containing fluoroalkyl amines and isocyanates

(51) International Patent Classification(s)
C07C 315/02 (2006.01) **C07C 319/20** (2006.01)
C07C 317/28 (2006.01) **C07C 323/25** (2006.01)
C07C 319/16 (2006.01) **C07C 331/20** (2006.01)
C07C 319/18 (2006.01) **C07D 207/27** (2006.01)

(21) Application No: **2008334034** (22) Date of Filing: **2008.12.01**

(87) WIPO No: **WO09/073592**

(30) Priority Data

(31) Number 12/273,091	(32) Date 2008.11.18	(33) Country US	
	61/005,241		US

(43) Publication Date: **2009.06.11**
(44) Accepted Journal Date: **2013.06.06**

(71) Applicant(s)
E. I. du Pont de Nemours and Company

(72) Inventor(s)
Warren, Hollis Thomas;Gonska, Brent Ryan;Herzog, Axel Hans-Joachim

(74) Agent / Attorney
Houlihan2, Level 1 70 Doncaster Road, BALWYN NORTH, VIC, 3104

(56) Related Art
US 6,288,051 B1
GB 1231952 A
US 6,780,855 B2

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 June 2009 (11.06.2009)

PCT

(10) International Publication Number
WO 2009/073592 A3

(51) International Patent Classification:

C07C 315/02 (2006.01) C07C 319/20 (2006.01)
C07C 317/28 (2006.01) C07C 323/25 (2006.01)
C07C 319/16 (2006.01) C07C 331/20 (2006.01)
C07C 319/18 (2006.01) C07D 207/27 (2006.01)

(74) Agent: MAYER, Nancy, S.; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(21) International Application Number:

PCT/US2008/085100

(22) International Filing Date:

1 December 2008 (01.12.2008)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/005,241 3 December 2007 (03.12.2007) US
12/273,091 18 November 2008 (18.11.2008) US

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HERZOG, Axel, Hans-Joachim [DE/US]; 703 Owen Road, West Chester, Pennsylvania 19380 (US). WARREN, Hollis, Thomas [US/US]; 1914 Sheldon Drive, Newark, Delaware 19711 (US). GONSKA, Brent, Ryan [US/US]; 6-3A Doe Run Court, Arundel Apartments, Wilmington, Delaware 19808 (US).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:

30 July 2009

(54) Title: SULFUR CONTAINING FLUOROALKYL AMINES AND ISOCYANATES

(57) Abstract: The present invention provides fluoroalkyl amines represented by the formula R₁-Q-S(O)_x-C(H)_y(CH₂)_{z+(1-1)}-NHR and fluoroalkyl isocyanates and isothiocyanates represented by the formula RrQ-S(O)x-C(H)y(CH₂)_{z+(1-1)}-N=C=X₁, where x is 1 or 2; z is 0 or 1; I is 1 or 2 and j is 0 or 1, such that i+j=2; R is chosen from H or a C₁ to C₄ alkyl and X₁ is O or S. Additionally, the invention provides a method for making a sulfur-containing fluoroalkyl amine comprising the steps of (a) reacting a thiol represented by R₁-Q-SH with a /V-vinylamide represented by H₂C=CH-(CH₂)_y-NR-C(O)-R to produce an amide intermediate represented by RrQ-S-C(H)_I(CH₃)J-(CH₂)_{z+(1-1)}-NR-C(O)-R; (b) optionally reacting the amide intermediate with an oxidizing agent to produce a sulfur oxide intermediate represented by RrQ-S(O)x-C(H)_I(CH₃)_J-(CH₂)_{z+(1-1)}-NR-C(O)-R and (c) subjecting the amide intermediate or the sulfur oxide intermediate to deacylation to produce the sulfur-containing fluoroalkyl amine.

A3

WO 2009/073592

SULFUR CONTAINING FLUOROALKYL AMINES AND ISOCYANATES

FIELD OF THE INVENTION

The present invention relates to sulfur containing fluoroalkyl
5 amines, methods for making the same, and isocyanate/isothiocyanate
derivatives of the same.

BACKGROUND OF THE INVENTION

Sulfur containing fluoroalkyl amines are useful as intermediates for
compounds which are in turn useful for imparting water and oil repellency
10 to textiles. Sulfur containing fluoroalkyl amines used in this manner may
be found in Example 8 of Rondestvedt et al. (U.S. Pat. No. 3,655,732)
wherein they are made by reacting an iodo-fluoroalkyl with an aminoalkyl
thiol. Specifically, Rondestvedt et al. teaches reacting $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{I}$
(an iodo-fluoroalkyl) with $\text{HS-CH}_2\text{CH}_2\text{-NH}_2$ (an aminoalkyl thiol) to make
15 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{-S-CH}_2\text{CH}_2\text{-NH}_2$ (a sulfur containing fluoroalkyl amine).

One disadvantage of preparing sulfur containing fluoroalkyl amines
according to the method disclosed by Rondestvedt et al. is that crude
product obtained by such a method can contain up to 29 mole percent of
impurities. To increase yield and reduce the amount of these impurities,
20 tert-butanol has been used as reaction solvent (*J. Org. Chem.* **1977**, 42,
2680 – 2683); however, tert-butanol is relatively expensive and
subsequent isolation of the product can be unpredictably tedious due to
foam and emulsion formation.

In addition to problems of poor yield, another disadvantage of
25 preparing sulfur containing fluoroalkyl amines according to the method
disclosed by Rondestvedt et al. is that such a method is incapable of
producing oxidized forms of sulfur containing fluoroalkyl amines. While
Rondestvedt et al. disclose a method of making sulfur containing
fluoroalkyl amines such as $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{-S-CH}_2\text{CH}_2\text{-NH}_2$, the method
30 of Rondestvedt et al. cannot produce corresponding oxidized forms such

09 May 2013

2008334034

as $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}(\text{O})-\text{CH}_2\text{CH}_2-\text{NH}_2$ or $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}(\text{O})_2-\text{CH}_2\text{CH}_2-\text{NH}_2$.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a method of making sulfur containing fluoroalkyl amines which overcomes the problems of previously known methods such as the one described by Rondestvedt. For example, unlike previously known methods, the method of the present invention can achieve higher yields of sulfur containing fluoroalkyl amines without resorting to costly solvents. Furthermore, unlike previously known methods, the method of the present invention can produce oxidized forms of sulfur containing fluoroalkyl amines wherein the sulfur atom thereof is oxidized.

In the method of the present invention, a fluoroalkyl thiol is reacted with a *N*-vinylamide resulting in an amide intermediate which is then subjected to deacylation to make corresponding sulfur containing fluoroalkyl amine. Optionally, the amide intermediate can be subjected to oxidation prior to deacylation thereby producing an oxidized form of sulfur containing fluoroalkyl amines wherein the sulfur atom thereof is oxidized.

Fluoroalkyl thiols useful in the present invention are represented by $\text{R}_f\text{Q}-\text{SH}$ wherein R_f is chosen from a) $(\text{CF}_3)_2\text{CF}$; b) $(\text{CF}_3)_2\text{CH}$, $\text{CF}_3(\text{CF}_2)_2\text{OCFHCF}_2$ or HC_mF_{2m} wherein m is 2 to 12; c) $\text{CF}_3(\text{CF}_2)_2\text{OCF}_2\text{CF}_2$, $\text{CF}_3(\text{CF}_2)_2\text{OCFHCF}_2$ or $\text{CF}_3\text{CF}_2\text{CF}_2[\text{OCF}(\text{CF}_3)\text{CF}_2]_m\text{OCR}^1\text{F}$ wherein m is an integer from 6 to 15 and R^1 is F, CF_3 or H; d) $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2\text{CF}_2)_m$ wherein m is 1, 2 or 3; and e) $\text{F}[(\text{CF}_2\text{CF}_2)_n(\text{CH}_2\text{CH}_2)_m]_k\text{CF}_2\text{CF}_2$ wherein $n = 1, 2$ or 3; $m = 1$ or 2; and $k = 1, 2$ or 3; Q is chosen from the group consisting of a C_2-C_{12} hydrocarbylene; x is 1 or 2; z is 0 or 1; i is 1 or 2; j is 0 or 1; provided that $i + j = 2$; and R is chosen from H and a C_1 to C_4 alkyl.

N-Vinylamides useful in the present invention are represented by $\text{H}_2\text{C}=\text{CH}-(\text{CH}_2)_y-\text{NR}-\text{C}(\text{O})-\text{R}$ wherein y is an integer chosen from 0 to 16, preferably 1, and most preferably 0; and each R is independently chosen from H or a C_1 to C_4 alkyl, preferably methyl, and most preferably H.

When the aforementioned fluoroalkyl thiols and the aforementioned *N*-vinylamides are reacted, in accordance with the present invention, the result is an amide intermediate of the present invention represented by R_f-

2008334034 09 May 2013

Q—S—C(H)_i(CH₃)_j—(CH₂)_{z+(i-1)}—NR—C(O)—R wherein each R is independently chosen from H or a C₁ to C₄ alkyl, preferably methyl, and most preferably H. More preferably, i = 1, j = 1, and z = 0. Still even more preferably, i = 2, j = 0, and z = 0.

Except where otherwise noted, the aforementioned definitions for R_f, Q, R, i, j, y and z are applied consistently throughout the specification and claims.

The amide intermediate of the present invention can be subjected to deacylation to produce a sulfur containing fluoroalkyl amine represented by R_f—Q—S—C(H)_i(CH₃)_j—(CH₂)_{z+(i-1)}—NHR wherein R is chosen from H or a C₁ to C₄ alkyl, preferably methyl, and most preferably H. Optionally, prior to removal of the acyl group, the amide intermediate of the present invention can be subjected to oxidation to produce a sulfur oxide intermediate of the present invention represented by R_f—Q—S(O)_x—C(H)_i(CH₃)_j—(CH₂)_{z+(i-1)}—NR—C(O)—R wherein x is 1 or 2. Except where otherwise noted, the aforementioned definition x is used consistently throughout the specification and claims. The sulfur oxide intermediate can then be subjected to deacylation to produce a sulfur containing fluoroalkyl amine of the present invention represented by R_f—Q—S(O)_x—C(H)_i(CH₃)_j—(CH₂)_{z+(i-1)}—NHR. Previously known methods were not capable of making sulfur containing fluoroalkyl amines having the —S(O)_x— moiety.

Advantageously, the amide intermediate of the present invention of the present invention represented by R_f—Q—S—C(H)_i(CH₃)_j—(CH₂)_{z+(i-1)}—NR—C(O)—R can be subjected to oxidation such that the sulfur atom thereof is selectively oxidized while the amide group, NR—C(O)—R, remains unoxidized. After oxidation, deacylation can be conducted to convert the amide group, NR—C(O)—R, into an amine group, —NHR, thereby resulting in a sulfur containing fluoroalkyl amine wherein the sulfur thereof is oxidized. Previously known methods do not form any intermediate wherein the sulfur atom thereof can be selectively oxidized. In contrast to

25

30

09 May 2013

2008334034

the present invention, previously known methods only make compounds wherein both a sulfur group, -S-, and an amine group, -NHR, are present thereby rendering the selective oxidation of the sulfur group impossible because of the potential oxidation of the amine group.

DETAILED DESCRIPTION OF THE INVENTION

Unless otherwise stated, the R_f moiety referred to throughout this disclosure is chosen from a) $(CF_3)_2CF$; b) $(CF_3)_2CH$, $CF_3(CF_2)_2OCFHCF_2$ or HC_mF_{2m} wherein m is 2 to 12; c) $CF_3(CF_2)_2OCF_2CF_2$, $CF_3(CF_2)_2OCFHCF_2$ or $CF_3CF_2CF_2[OCF(CF_3)CF_2]_mOCR^1F$ wherein m is an integer from 6 to 15 and R^1 is F, CF_3 or H; d) $CF_3(CF_2)_5(CH_2CF_2)_m$ wherein m is 1, 2 or 3; and e) $F[(CF_2CF_2)_n(CH_2CH_2)_m]_kCF_2CF_2$ wherein n = 1, 2 or 3; m = 1 or 2; and k = 1, 2 or 3.

Unless otherwise stated, the term "fluoroalkyl thiol" or "thiol" as used throughout this disclosure means a compound represented by R_f-Q-SH wherein Q is chosen from the group consisting of a C_2-C_{12} hydrocarbylene.

2008334034 09 May 2013

The fluoroalkyl thiols useful in the present invention can be made by any known method. For example, Lantz (U.S. Pat. No. 4,845,300) discloses the following reaction scheme for making thiols useful for the present invention: $R_fCH_2CH_2I + S=C(NH_2)_2 \rightarrow [R_fCH_2CH_2S-(NH_2)_2]^+ I^- + NaOH$ $\rightarrow R_fCH_2CH_2SH + NaI + O=C(NH_2)_2 + MeOH$ wherein R_f is defined therein. Alternatively, Jacobson (U.S. Pat. No. 5,728,887) discloses hydrogenation for making thiols useful for the present invention: $R_fCH_2CH_2SCN + H_2 \rightarrow R_fCH_2CH_2SH + HCN$ wherein R_f is defined therein. Alternatively, a thioacetate intermediate (*J. Fluorine Chem.* 2000, 104, 173 -183) can be used according to the following reaction: $R_fCH_2CH_2I + KSOCMe \rightarrow$ (saponification) $\rightarrow R_fCH_2CH_2SH + KOAc$.

Unless otherwise stated, the *N*-vinylamides referred to throughout this disclosure and useful in the present invention are represented by $H_2C=CH-(CH_2)_y-NR-C(O)-R$ wherein y is an integer chosen from 0 to 16, preferably 1, and most preferably 0; and each R is independently chosen from H or a C_1 to C_4 alkyl, preferably methyl, and most preferably H. *N*-Vinylamides useful in the present invention include well known compounds which are commercially available such as *N*-vinylformamide, *N*-vinylacetamide, *N*-vinyl-*N*-methyl-acetamide, *N*-vinyl pyrrolidone, and *N*-allyl formamide.

25 In the method of the present invention, a fluoroalkyl thiol is reacted with a *N*-vinylamide resulting in an amide intermediate which is then subjected to deacylation to make a corresponding sulfur containing fluoroalkyl amine. Optionally, the amide intermediate can be subjected to oxidation prior to deacylation thereby producing an oxidized form of sulfur containing fluoroalkyl amines wherein the sulfur atom thereof is oxidized.

30 Unless otherwise stated, the amide intermediates referred to throughout this disclosure are represented by $R_f-Q-S-C(H)(CH_3)-(CH_2)_{z+(i-1)}-NR-C(O)-R$ wherein each R is independently chosen from H or a C_1 to C_4 alkyl, preferably, methyl, and most preferably, H. The amide intermediates of the present invention are made by reacting a fluoroalkyl thiol, $R_f-Q-S H$, with a *N*-vinylamide, $H_2C=CH-(CH_2)_y-NR-C(O)-R$.

Specifically, the amide intermediates of the present invention can be made by the free-radical addition of a fluoroalkyl thiol, R_f-Q-SH , to a *N*-vinylamide, $H_2C=CH-(CH_2)_y-NR-C(O)-R$. Reaction conditions for free-radical conditions are well known in the art. An example of a method for 5 conducting free-radical addition involves dissolving one equivalent of a chosen thiol, one equivalent of a chosen *N*-vinylamide, and an initiator. The solution is then heated to a temperature (typically about 65 °C) which activates the reaction which is stirred until complete consumption of the thiol as determined by gas chromatography-mass spectrometry (GC/MS) 10 monitoring.

Useful initiators for free-radical addition are well known in the art and include: azo compounds, such as azobisisobutyronitrile and azo-2-cyanovaleric acid; hydroperoxides, such as cumene, t-butyl and t-amyl hydroperoxide; dialkyl peroxides, such as di-t-butyl and dicumylperoxide; 15 peroxyesters, such as t-butylperbenzoate and di-t-butylperoxy phthalate; and diacylperoxides, such as benzoyl peroxide and lauryl peroxide; peroxide such as persulfate; and metals such copper. Examples of useful organic solvents for free-radical addition include: ethers, such as tetrahydrofuran, dimethoxyethane, 1,4-dioxane; acetates, such as ethyl acetate, butyl acetate, and isopropyl acetate; alcohols, such as 2-methanol, ethanol, methylpropan-2-ol, isopropanol, 2-methoxyethanol 20 (monoglyme), 2-methoxypropan-2-ol; and ketones, such as acetone, methylisobutyl ketone, and methylethyl ketone, such as N-methyl-2-pyrrolidone, and mixtures thereof. Also hydrocarbon solvents such as 25 toluene are suitable.

As an alternative to free-radical addition, the amide intermediates of the present invention can be made by the Michael addition of a fluoroalkyl thiol, R_f-Q-SH , to a *N*-vinylamide, $H_2C=CH-(CH_2)_y-NR-C(O)-R$, using catalytic amounts of a base, such as tertiary ammonium hydroxide or 30 sodium hydride.

The sulfur oxide intermediates of the present invention are made by the oxidation of an amide intermediate using an oxidizing agent, such as

peroxides. The oxidation may optionally include catalysts such as sodium tungstate, phenyl phosphonate, trioctylmethyl ammonium bisulfate, and mixtures thereof. When such catalysts are used during oxidation, the $-\text{S(O)}_x-$ moiety of the resulting sulfur oxide intermediate is $-\text{S(O)}_2-$. One example us the use of such catalyst is in *Tetrahedron* **2005**, *61*, 8315 - 8327 and Sato et al. reference [27] therein. When no catalysts are used during oxidation, the $-\text{S(O)}_x-$ moiety of the resulting sulfur oxide intermediate is $-\text{S(O)}-$. An example of a method for conducting oxidation of an amide intermediate involves adding about one mol equivalent of an oxidizing agent (preferably hydrogen peroxide) to about one mol equivalent of an amide intermediate (optionally in the presence of catalyst) in solvent (preferably an alcohol such as ethanol) at a low temperature (typically about 0 °C) and stirring the mixture while allowing to warm (typically to about 50-60 °C) to activate the oxidation reaction. The progress of the reaction can be monitored via gas chromatography. Upon complete conversion (about 5 hours) any excess oxidizing agent is destroyed; for example hydrogen peroxide can be destroyed with a solution of sodium sulfite. The solvent can then be removed by distillation and the resulting residue containing crude product can be washed (e.g. with water) and dried in vacuum.

The sulfur containing fluoroalkyl amines of the present invention can be made by deacylation of an amide intermediate or a sulfur oxide intermediate. Deacylation of an amide intermediate can be performed by acid catalyzed or base catalyzed deacylation. Deacylation of a sulfur oxide intermediate can be performed by acid catalyzed deacylation.

Acid catalyzed deacylation can be conducted by adding to an amide intermediate or a sulfur oxide intermediate in solvent (preferably an alcohol such as ethanol) at a low temperature (typically 0 °C), a molar excess (typically about a six-fold excess) of concentrated acid (e.g. hydrochloric acid). This mixture is stirred and allowed to warm to ambient temperature and after an initial formation of foam the reaction mixture is slowly heated and held at reflux temperature (about 85 °C) for about 5

hours. The progress of the reaction can be monitored via gas chromatography. Upon complete conversion, the pH of the solution is brought to about 8-10 by carefully adding aqueous base (e.g. sodium hydroxide solution). The resulting sulfur containing fluoroalkyl amine in 5 crude form separates as a bottom layer and can be isolated, e.g. with a separatory funnel. Alternatively, if the ammonium salt is desired, no aqueous base is added.

Base catalyzed deacylation can be conducted by adding an excess (typically about a five-fold excess) of concentrated base (e.g. sodium 10 hydroxide) to the amide intermediate in solvent (preferably an alcohol such as ethanol) at a low temperature (typically 0 °C). This mixture is stirred and allowed to warm to ambient temperature and the reaction mixture is slowly heated and held at reflux temperature (about 85 °C) for about 8 hours. The progress of the reaction can be monitored via gas 15 chromatography. The resulting sulfur containing fluoroalkyl amine in crude form separates as a bottom layer and can be isolated, e.g. via a separatory funnel.

One of the advantages of the formation of an amide intermediate of the present invention, $R_f-Q-S-C(H)_i(CH_3)_j-(CH_2)_{z+(i-1)}-NR-C(O)-R$, is that 20 the sulfur atom therein can be selectively oxidized while the acyl group – $C(O)-R$ is remains unoxidized thereby forming a sulfur oxide intermediate represented by $R_f-Q-S(O)_x-C(H)_i(CH_3)_j-(CH_2)_{z+(i-1)}-NR-C(O)-R$ wherein x is 1 or 2. The sulfur oxide intermediate can then be subjected to deacylation to convert the amide group, $NR-C(O)-R$, into an amine group, 25 – NHR , thereby resulting in a sulfur containing fluoroalkyl amine wherein the sulfur thereof is oxidized. Previously known methods do not form any intermediate wherein the sulfur atom thereof can be selectively oxidized. In contrast to the present invention, previously known methods only make compounds wherein both a sulfur group – $S-$ and an amine group – NHR 30 (R is chosen from H or a C_1 to C_4 alkyl, preferably methyl, and most preferably H) are present thereby rendering the selective oxidation of the

09 May 2013

2008334034

sulfur group impossible because of the potential oxidation of the amine group.

Accordingly, it was previously unknown how to make a sulfur containing fluoroalkyl amine of the present invention represented by $R_f-Q-S(O)_x-CH_2-C(H)_i(CH_3)_j-(CH_2)_{z+(i-1)}-NH_2$ wherein:

R_f is chosen from a) $(CF_3)_2CF$; b) $(CF_3)_2CH$, $CF_3(CF_2)_2OCFHCFC_2$ or HC_mF_{2m} wherein m is 2 to 12; c) $CF_3(CF_2)_2OCF_2CF_2$, $CF_3(CF_2)_2OCFHCFC_2$ or $CF_3CF_2CF_2[OCF(CF_3)CF_2]_mOCR^1F$ wherein m is an integer from 6 to 15 and R^1 is F, CF_3 or H; d) $CF_3(CF_2)_5(CH_2CF_2)_m$ wherein m is 1, 2 or 3; and e) $F[(CF_2CF_2)_n(CH_2CH_2)_m]_kCF_2CF_2$ wherein n = 1, 2 or 3; m = 1 or 2; and k = 1, 2 or 3;

Q is chosen from the group consisting of a C_2-C_{12} hydrocarbylene;
 x is 1 or 2;
 z is 0 or 1;
 i is 1 or 2, j is 0 or 1; provided that $i + j = 2$.

It was also previously unknown how to make isocyante and isothiocyanate derivatives of the sulfur containing fluoroalkyl amine of the present invention, said isocyante and isothiocyanate derivatives represented by $R_f-Q-S(O)_x-C(H)_i(CH_3)_j-(CH_2)_{z+(i-1)}-N=C=X^1$ wherein:

X^1 is O or S;

R_f is chosen from a) $(CF_3)_2CF$; b) $(CF_3)_2CH$, $CF_3(CF_2)_2OCFHCFC_2$ or HC_mF_{2m} wherein m is 2 to 12; c) $CF_3(CF_2)_2OCF_2CF_2$, $CF_3(CF_2)_2OCFHCFC_2$ or $CF_3CF_2CF_2[OCF(CF_3)CF_2]_mOCR^1F$ wherein m is an integer from 6 to 15

09 May 2013

2008334034

and R¹ is F, CF₃ or H; d) CF₃(CF₂)₅(CH₂CF₂)_m wherein m is 1, 2 or 3; and e) F[(CF₂CF₂)_n(CH₂CH₂)_m]_kCF₂CF₂ wherein n = 1, 2 or 3; m = 1 or 2; and k = 1, 2 or 3;

Q is chosen from the group consisting of a C₂—C₁₂ hydrocarbylene; and

x is 1 or 2;

z is 0 or 1;

i is 1 or 2, j is 0 or 1; provided that i + j = 2.

Isocyante and isothiocyanate derivatives of the sulfur containing fluoroalkyl amine of the present invention can be made by any suitable process which converts a primary amine group (-NH₂) to an

isocyanate group (-N=C=O) or isothiocyanate group (-N=C=S). An example of a method of converting a primary amine group (-NH₂) to an isocyanate group (-N=C=O) may be found in Kornek et al. (DE10108543) consistent with the following reaction scheme: R_f-CH₂CH₂-S-CH₂CH₂-

5 NH₂ + EtOC(O)Cl + Cl₃SiMe + 2 NEt₃ → R_f-CH₂CH₂-S-CH₂CH₂-N=C=O + EtOSi(Me)Cl₂ + 2 Et₃NHCl. An example of a method of converting a primary amine group (-NH₂) to an isothiocyanate group (-N=C=S) may be found in *J. Org. Chem.* **1956**, 21, 404-405 consistent with the following reaction scheme: R_f-CH₂CH₂-S-CH₂CH₂-NH₂ + CS₂ + EtOC(O)Cl + 2 NEt₃

10 → R_f-CH₂CH₂-S-CH₂CH₂-N=C=S + COS + EtOH + 2 Et₃NHCl.

Examples

Table 1 below shows the fluoroalkyl thiols used throughout the examples numbered as Thiol #1, Thiol #2, and Thiol #3. Table 2 below shows amide intermediates made from the thiols in Table 1. Table 3

15 shows sulfur oxide intermediates made from the amide intermediates of Table 2. Table 4 shows sulfur containing fluorinated amines made from the amide intermediates or sulfur oxide intermediates which are labeled Fluorinated Amine #1, Fluorinated Amine #2, Fluorinated Amine #3, and Fluorinated Amine #4. Table 4 also shows a sulfur containing fluorinated

20 amine salt labeled Fluorinated Amine Salt #1. Table 4 further shows isocyanate and isothiocyanate derivatives which respectively labeled Fluorinated Isocyanate #1 and Fluorinated Isothiocyanate #1.

Table 1

Thiol	IUPAC Name	Structure
Thiol #1	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-thiol	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SH}$
Thiol #2	3,3,4,4-tetrafluoro-4-heptafluoropropoxy-butane-1-thiol	$\text{CF}_3(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{SH}$
Thiol #3	3,3,5,5,6,6,7,7,8,8,8-undecafluoro-octane-1-thiol	$\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CF}_2(\text{CH}_2)_2\text{SH}$

Table 2

Amide Intermediate	Structure	Made from this Thiol	Made from this N-vinyl amide
Amide Intermediate #1A	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{O})-\text{CH}_3$	Thiol #1	$\text{CH}_2=\text{CH}-\text{NH}-\text{C}(\text{O})-\text{CH}_3$
Amide Intermediate #1B(*)	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)-\text{C}(\text{O})-\text{CH}_3$ $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}(\text{CH}_3)-\text{N}(\text{CH}_3)-\text{C}(\text{O})-\text{CH}_3$	Thiol #1	$\text{CH}_2=\text{CH}-\text{N}(\text{CH}_3)-\text{C}(\text{O})-\text{CH}_3$
Amide Intermediate #1C	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{O})-\text{H}$	Thiol #1	$\text{CH}_2=\text{CH}-\text{NH}-\text{C}(\text{O})-\text{H}$
Amide Intermediate #1D	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)-\text{C}(\text{O})-\text{H}$	Thiol #1	$\text{H}_2\text{C}=\text{CH}-\text{N}(\text{CH}_3)-\text{C}(\text{O})-\text{H}$
Amide Intermediate #2	$\text{CF}_3(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{O})-\text{H}$	Thiol #2	$\text{CH}_2=\text{CH}-\text{NH}-\text{C}(\text{O})-\text{H}$
Amide Intermediate #3	$\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CF}_2(\text{CH}_2)_2\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{O})-\text{H}$	Thiol #3	$\text{CH}_2=\text{CH}-\text{NH}-\text{C}(\text{O})-\text{H}$

* isomeric mixture of *N*-methyl-*N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octylsulfanyl)-ethyl]-acetamide and (*R,S*)-*N*-methyl-*N*-(1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octylsulfanyl)-ethyl]-acetamide

Table 3

Sulfur oxide intermediate	Structure	Made from oxidation of Amide Intermediate
Sulfur oxide intermediate #1A	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}(\text{O})-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{O})-\text{H}$	Amide Intermediate #1C
Sulfur oxide intermediate #1B	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}(\text{O})_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{O})-\text{H}$	Amide Intermediate #1C

Table 4

Ex.	Product	Structure	Intermediate used to make product
1			Amide Intermediate #1A *
2	Fluorinated Amine #1	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	Amide Intermediate #1C *
3			Amide Intermediate #1A **
4			Amide Intermediate #1C **
5	Fluorinated Amine #2	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}(\text{O})-\text{CH}_2-\text{CH}_2-\text{NH}_2$	Sulfur oxide intermediate #1A *
6	Fluorinated Amine #3	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}(\text{O})_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	Sulfur oxide intermediate #1B *
7	Fluorinated Amine #4	$\text{CF}_3(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	Amide Intermediate #2 *
8	Fluorinated Amine Salt #1	$[\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CF}_2(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+] \text{Cl}^-$	Amide Intermediate #3
9	Fluorinated Isocyanate #1	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{N}=\text{C}=\text{O}$	Fluorinated Amine #1
10	Fluorinated Isothiocyanate #1	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{N}=\text{C}=\text{S}$	Fluorinated Amine #1

*made by procedure for acid catalyzed deacylation **made by procedure for base catalyzed deacylation

Thiol #1

Thiol #1 was 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-thiol which was made as follows. Under nitrogen thiourea (1.1 equivalents) and 1-iodo-2-perfluorohexylethane (1 equivalent) were added to a degassed mixture of dimethoxyethane (DME, 9 parts) and water (1 part). The reaction mixture was held at reflux temperature for 8 hours. Most of the DME was distilled off and the distillation residue was allowed to cool to ambient temperature. Under stirring a solution of sodium methoxide in methanol (1 molar, 1.1 equivalents) was added to the suspension. Degassed water was added to the mixture. Thiol #1 was collected quantitatively as the fluorous bottom layer.

The spectroscopical data for the product were in agreement with those published elsewhere (*J. Fluorine Chem.* **1985**, 28, 341 – 355 and *J. Fluorine Chem.* **1989**, 42, 59 – 68).

15 Thiol #2

Thiol #2 was 3,3,4,4-tetrafluoro-4-heptafluoropropoxy-butane-1-thiol which was made as follows. 1,1,1,2,2,3,3-heptafluoro-3-[(1,2,2-trifluoroethenyl)oxy]-propane (available from E. I. du Pont de Nemours and Company as PPVE) was reacted with iodine monochloride and subsequently treated with boron trifluoride to furnish 1,1,1,2,2,3,3-heptafluoro-3-[(1-iodo-1,1,2,2-trifluoroethenyl)oxy]-propane (US5481028A). 1,1,1,2,2,3,3-Heptafluoro-3-[(1-iodo-1,1,2,2-trifluoroethenyl)oxy]-propane was then reacted with ethylene in the presence of a peroxide initiator to yield 1,1,2,2-tetrafluoro-1-(1,1,2,2,3,3,3-heptafluoropropoxy)-4-iodo-butane (US20080113199A1). Under nitrogen, thiourea (1.1 equivalents) and 1,1,2,2-tetrafluoro-1-(1,1,2,2,3,3,3-heptafluoropropoxy)-4-iodo-butane were added to degassed 1,4-dioxane. The reaction mixture was heated at reflux temperature for 8 hours. The dioxane was distilled off and the distillation residue was allowed to cool to ambient temperature. Under stirring, a thoroughly degassed solution of sodium hydroxide in methanol and water 1:1 (1 molar, 1.1 equivalents) was added to the suspension. The mixture was

heated at 50-60 °C for 5 hours. Additional degassed water was added to the mixture. Thiol #2 was collected quantitatively as the fluorous bottom layer and purified via distillation. NMR of Thiol #2 was obtained as follows.

5 $^1\text{H-NMR}$ (CDCl_3): 1.60 (t, $J = 17$ Hz, 1H, SH), 2.45 (m, 2H, CF_2CH_2), 2.86 (m, 2H, CH_2S).

Thiol #3

Thiol #3 was 3,3,5,5,6,6,7,7,8,8,8-undecafluoro-octane-1-thiol which was made as follows. Under nitrogen, potassium thioacetate (1.1 equivalents) was added to a solution of 1,1,1,2,2,3,3,4,4,6,6-undecafluoro-8-iodo-octane (1 equivalent) in THF. The reaction mixture was stirred at 10 50 ° for 5 hours. The THF was removed under reduced pressure. The distillation residue was dissolved in methanol (25 mL/0.1 mol) and treated with hydrochloric acid (37 w/% in water, three fold excess). Additional 15 degassed water was added to the mixture. Thiol #3 was collected as the fluorous bottom layer and purified via distillation. NMR of Thiol #3 was obtained as follows.

$^1\text{H-NMR}$ (CDCl_3): 1.55 (s, br, 1H, SH), 2.32 (m, 2H, CF_2CH_2), 2.74 (m, 4H, CH_2S and $\text{CF}_2\text{CH}_2\text{CF}_2$).

20 Table 1

The following table shows the thiols that were made above.

Thiol #1

Procedure for Amide Intermediate Synthesis

When amide intermediate synthesis was used to make a chosen amide intermediate in the examples below, amide intermediate synthesis was conducted in the following manner. All amide intermediates in the examples were made according to the following procedure. A solution of one equivalent of a chosen thiol, one equivalent of a chosen *N*-vinylamide, and 0.04 parts (mol equivalents) VAZO 64 (available from E. I. du Pont de Nemours and Company of Wilmington, Delaware, USA) in inhibitor-free tetrahydrofuran (THF) was slowly warmed to 65 °C. At about 45 °C an

exotherm occurred, increasing the reaction temperature briefly to 70 °C. The reaction was stirred at 65 °C until complete consumption of the thiol was indicated as determined by gas chromatography-mass spectrometry (GC/MS) monitoring for 5 hours.

5 Amide Intermediate #1A

Amide Intermediate #1A was *N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8,8-tridecafluoro-octylsulfanyl)-ethyl]-acetamide which was made using amide intermediate synthesis wherein Thiol #1 was the chosen thiol and *N*-vinylacetamide was the chosen *N*-vinylamide. All volatiles were removed under reduced pressure to furnish the desired crude amide free of its regioisomer as a light orange oil. NMR of Amide Intermediate #1A was obtained as follows.

¹H-NMR (CDCl₃): 1.98 (s, 3H, COCH₃), 2.36 (m, 2H, CF₂CH₂), 2.70 (m, 4H, CH₂SCH₂), 3.43 (m, 2H, CH₂N), 5.98 (s, br, 1H, NH).

15 Amide Intermediate #1B

Amide Intermediate #1B was an isomer mixture of *N*-methyl-*N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octylsulfanyl)-ethyl]-acetamide (**I**) and (R,S)-*N*-methyl-*N*-[1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octylsulfanyl)-ethyl]-acetamide (**II**) which was made using amide intermediate synthesis wherein Thiol #1 was the chosen thiol and *N*-vinyl-*N*-methyl-acetamide was the chosen *N*-vinylamide. All volatiles were removed under reduced pressure to furnish crude Amide Intermediate #1B as a mixture of regioisomers of **I** and **II** (3:2) as a light orange oil. The crude Amide Intermediate #1B was about 99% pure and was suitable for further use without further purification. The isomers were not separated.

NMR of Amide Intermediate #1B was obtained as follows.

¹H-NMR (CDCl₃): (**I**): 1.98 (s, 3H, COCH₃), 2.35 (m, 2H, CF₂CH₂), 2.68 (m, 4H, CH₂SCH₂), 2.96 (s, 3H, NCH₃), 3.47 (m, 2H, CH₂N); (**II**): 2.03 (s, 3H, COCH₃), 2.35 (m, 2H, CF₂CH₂), 2.65 (m, 5H, CF₂CH₂CH₂S and CHCH₃), 2.80 (s, 3H, NCH₃), 3.43 (m, 1H, CHN).

Amide Intermediate #1C

Amide Intermediate #1C was *N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octylsulfanyl)-ethyl]-formamide which was made using amide intermediate synthesis wherein Thiol #1 was the chosen thiol and *N*-vinylformamide was the chosen *N*-vinylamide. All volatiles were removed under reduced pressure to furnish the desired amide as an off-white solid. NMR of Amide Intermediate #1C was obtained as follows.

¹H-NMR (CDCl₃): 2.33 (m, 2H, CF₂CH₂), 2.70 (m, 4H, CH₂SCH₂), 3.39 (m, 1H, 3.42 (m, 2H, CH₂N), 6.66 (s, br, 1H, NH), 8.12 (s, 1H, CHO).

Amide Intermediate #1D

Amide Intermediate #1D was 1-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octylsulfanyl)-ethyl]-pyrrolidin-2-one which was made using amide intermediate synthesis wherein Thiol #1 was the chosen thiol and *N*-vinylpyrrolidone was the chosen *N*-vinylamide. All volatiles were removed under reduced pressure to furnish the desired amide as an off-white solid (Mp 64 °C). NMR of Amide Intermediate #1D was obtained as follows.

¹H-NMR (CDCl₃): 2.02 (m, 2H, CH₂CH₂CH₂), 2.37 (m, 4H, CF₂CH₂ and CH₂C=O), 2.71 (m, 2H, SCH₂CH₂N), 2.77 (m, 2H, CF₂CH₂CH₂S), 3.41 (m, 1H, 3.42 (m, 2H, SCH₂CH₂N), 3.48 (m, 1H, 3.42 (m, 2H, NCH₂CH₂CH₂).

Examples 1-4

In examples 1-4 below, Fluorinated Amine #1 was 2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octylsulfanyl)-ethylamine and was made by the deacylation of an amide intermediate as indicated. The NMR obtained in the examples below for Fluorinated Amine #1 is represented as follows.

¹H-NMR (CDCl₃): 1.28 (br, 2H, NH₂), 2.38 (m, 2H, CF₂CH₂), 2.65 (m, 2H, SCH₂), 2.73 (m, 2H, CH₂S), 2.89 (m, 2H, CH₂N).

¹H-NMR (DMSO-d₆): 1.46 (br, 2H, NH₂), 2.48 (m, 2H, CF₂CH₂), 2.58 (m, 2H, SCH₂), 2.72 (m, 4H, CH₂S and CH₂N).

¹³C-NMR (CDCl₃): 22.3 (s, CH₂S), 32.1 (m, CF₂CH₂), 35.8 (s, SCH₂), 40.5 (s, CH₂N).

5 Procedure for Acid Catalyzed Deacylation

When acid catalyzed deacylation was used to make a chosen fluorinated amine in the examples below, acid catalyzed deacylation was conducted in the following manner. Concentrated hydrochloric acid solution (37.5 w% in water, five to six-fold molar excess) was added to a 10 solution of one equivalent of a chosen amide intermediate in ethanol at 0 °C. The reaction mixture was allowed to warm to ambient temperature while being stirred. After the initial foam formation ceased the reaction mixture was slowly heated and held at reflux temperature for 5 hours at about 85 °C. The progress of the reaction was monitored via Gas 15 Chromatography. Upon complete conversion, the pH of the solution was brought to 8-10 by carefully adding aqueous sodium hydroxide solution. The chosen fluorinated amine in crude form separated as the bottom layer and was isolated as a brownish slightly viscous liquid via a separatory funnel. The aqueous phase was extracted with diethyl ether. The residue 20 of the dried ether phase was combined with the initial first crop. The chosen fluorinated amine in crude form was washed with water and dried using molecular sieves (4 Å) and was purified by distillation to obtain a colorless liquid in 80 to 95% yield as either a colorless solid or pale yellow liquid.

25 Example #1

Fluorinated Amine #1 was made by the acid catalyzed deacylation of Amide Intermediate #1A.

Example #2

Fluorinated Amine #1 was made by the acid catalyzed deacylation 30 of Amide Intermediate #1C.

Procedure for Base Catalyzed Deacylation

When base catalyzed deacylation was used to make a chosen fluorinated amine in the examples below, base catalyzed deacylation was conducted in the following manner. An aqueous solution of sodium hydroxide (five equivalents) was added to one equivalent of the chosen fluorinated amine at ambient temperature and the mixture was slowly brought to reflux temperature. After about 8 hours of reaction time, the chosen fluorinated amine in crude form separated as the bottom layer and was isolated as a brownish slightly viscous liquid via a separatory funnel.

5 It was washed with water and dried using molecular sieves (4 Å). The chosen fluorinated amine in crude form was purified by distillation and obtained as a colorless liquid in 80 to 95% yield as either a colorless solid or a pale yellow liquid.

10

Example #3

15 Fluorinated Amine #1 was made by the base catalyzed deacylation of Amide Intermediate #1A.

Example #4

Fluorinated Amine #1 was made by the base catalyzed deacylation of Amide Intermediate #1C.

20 Sulfur oxide intermediate #1A

Sulfur oxide intermediate #1A was *N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-sulfinyl)-ethyl]-formamide which was made by oxidation of Amide Intermediate #1C as follows. Hydrogen peroxide (35 w/% in water, 1.1 mol equivalents) was added to a solution of one equivalent of Amide Intermediate #1C in ethanol at 0 °C. The reaction mixture was allowed to warm to ambient temperature while being stirred. The progress of the reaction was monitored via Gas Chromatography. Upon complete conversion (5 hours) any excess peroxide was destroyed by adding a solution of sodium sulfite (negative peroxide test). The 25 ethanol was distilled off; the residue was washed with water and dried in

vacuum. The Sulfur oxide intermediate #1 was obtained quantitatively as a colorless solid. Mp 179 °C. NMR of Sulfur oxide intermediate #1A was obtained as follows.

¹H-NMR (CDCl₃): 2.59 (m, 2H, CF₂CH₂), 2.93 (dm, J = 170Hz, 2H,

5 SOCH₂CH₂N), 2.96 (m, 2H, CF₂CH₂CH₂SO), 3.84 (m, 2H, CH₂N), 6.50 (s, br, 1H, NH), 8.19 (s, 1H, CHO).

¹³C-NMR Spectrum of Sulfur oxide intermediate #1A could not be obtained due to its insufficient solubility most common organic deuterated solvents.

Sulfur oxide intermediate #1B

10 Sulfur oxide intermediate #1B was *N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-sulfonyl)-ethyl]-formamide which was made by oxidation of Amide Intermediate #1C as follows. A solution of sodium tungstate (0.01 equivalents), phenyl phosphonate (0.01 equivalents), and trioctylmethyl ammonium bisulfate (0.01 equivalents) in hydrogen peroxide (35 w/% in water, 2.2 equivalents) was prepared. This solution was slowly added to a solution of one equivalent of Amide Intermediate #1C in 15 ethanol at 0 °C. The reaction mixture was allowed to warm to ambient temperature and then heated to 60 °C while being stirred. The progress of the reaction was monitored via Gas Chromatography. Upon complete conversion any excess peroxide was destroyed by adding a solution of sodium sulfite (negative peroxide test). The ethanol was removed under reduced pressure. The residue was washed with water and dried in 20 vacuum. Sulfur oxide intermediate #1B was obtained quantitatively as a colorless solid. Mp 108 °C. NMR of Sulfur oxide intermediate #1B was obtained as follows.

¹H-NMR (CDCl₃): 2.62 (m, 2H, CF₂CH₂), 3.28 (m, br, 4H, CH₂SO₂CH₂), 3.83 (m, br, 2H, CH₂N), 6.25 (s, br, 1H, NH), 8.19 (s, 1H, CHO).

¹³C-NMR (CDCl₃): 22.3 (s, CF₂CH₂), 33.3 (s, CH₂N), 43.4 (s, SO₂CH₂), 51.6 (s, CH₂SO₂), 161.7 (s, CHO).

Example 5

Fluorinated Amine #2 was (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-sulfinyl)-ethylamine which was made by acid catalyzed deacylation of Sulfur oxide intermediate #1A. After acid deacylation, the 5 crude Fluorinated Amine #2 was filtered, washed with water, and dried. The drying step is important because Fluorinated Amine #2 forms adducts with both polar protic and non-protic solvents, respectively. Ethanol was removed from the filtrate under reduced pressure and the residue was washed with water and dried in vacuum. Fluorinated Amine #2 was 10 obtained quantitatively as a colorless solid. Mp > 250 °C. NMR of Fluorinated Amine #2 was obtained as follows. NMR analysis was performed on crystals obtained from dimethoxyethane (DME) with the following results.

15 $^1\text{H-NMR}$ (DMSO-d₆): 2.59 (m, 2H, CF₂CH₂), 2.80 (m, 2H, CH₂N), 2.88 (m, 2H, SOCH₂), 2.98 (m, 2H, CH₂SO).

Example 6

Fluorinated Amine #3 was 2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-sulfonyl)-ethylamine which was made by acid catalyzed deacylation of Sulfur oxide intermediate #1B as follows. Example 5 was 20 duplicated except Sulfur oxide intermediate #1B was used instead of Sulfur oxide intermediate #1A. Fluorinated Amine #3 was obtained quantitatively as a colorless solid, mp >250 °C. NMR (in CDCl₃) and IR analysis was performed on crystals obtained from dimethoxyethane (DME) with the following results.

25 $^1\text{H-NMR}$ (CDCl₃): 1.76 (br, 2H, NH₂), 2.68 (m, 2H, CF₂CH₂), 3.14 (m, 2H, CH₂N), 3.28 (m, 2H, SO₂CH₂), 3.39 (m, 2H, CH₂SO₂), 3.63 (m, 4H, OCH₃), 3.75 (m, 4H, OCH₂).

$^1\text{H-NMR}$ (DMSO-d₆): 2.71 (m, 2H, CF₂CH₂), 2.97 (m, 2H, CH₂N), 3.27 (m, 2H, SO₂CH₂), 3.52 (m, 2H, CH₂SO₂).

¹³C-NMR (CDCl₃): 24.5 (s, CF₂CH₂), 36.2 (m, CH₂SO₂), 43.1 (s, CH₂N), 46.6 (s, SO₂CH₂), 56.8, 61.9, 71.3, 72.5 (s, DME).

IR Spectrum: 1070 cm⁻¹ (sym. SO₂).

Amide Intermediate #2

5 Amide Intermediate #2 was *N*-[2-(3,3,4,4-tetrafluoro-4-heptafluoropropoxy-butylsulfanyl)-ethyl]-formamide was made using amide intermediate synthesis wherein Thiol #2 was the chosen thiol and *N*-vinylformamide was the chosen *N*-vinylamide. All volatiles were removed under reduced pressure to furnish the desired crude amide
10 quantitatively with a purity of 97% as an off-white solid. Mp >250 °C.

¹H-NMR (CDCl₃): 2.38 (m, 2H, CF₂CH₂), 2.77 (m, 4H, CH₂SCH₂), 3.53 (m, 2H, CH₂N), 6.88 (s, br, 1H, NH), 8.20 s, 1H, CHO).

Example 7

15 Fluorinated Amine #4 was 2-(3,3,4,4-tetrafluoro-4-heptafluoropropoxy-butylsulfanyl)-ethylamine which was made by acid catalyzed deacylation of Amide Intermediate #2. NMR analysis was performed on crystals obtained from dimethoxyethane (DME) with the following results.

20 ¹H-NMR (CDCl₃): 1.92 (br, 2H, NH₂), 2.32 (m, 2H, CF₂CH₂), 2.65 (t, 2H, SCH₂), 2.73 (m, 2H, CH₂S), 2.92 (t, 2H, CH₂N).

Amide Intermediate #3

25 Amide Intermediate #3 was *N*-[2-(3,3,5,5,6,6,7,7,8,8,8-udecafluoro-octylsulfanyl)-ethyl]-formamide which was made using amide intermediate synthesis wherein Thiol #3 was the chosen thiol and *N*-vinylformamide was the chosen *N*-vinylamide. All volatiles were removed under reduced pressure to furnish Amide Intermediate #3 quantitatively with a purity of 97% as an off-white solid. Mp >250 °C. NMR of Amide Intermediate #3 was obtained as follows.

¹H-NMR (CDCl₃): 2.33(m, 2H, CF₂CH₂), 2.73(m, 6H, CH₂SCH₂ and CF₂CH₂CF₂), 3.54 (m, 2H, CH₂N), 6.16 (s, br, 1H, NH), 8.19 (s, 1H, CHO).

Example 8

Fluorinated Amine Salt #1 was 2-(3,3,5,5,6,6,7,7,8,8,8-5 undecafluoro-octylsulfanyl)-ethyl-ammonium chloride which was made by the deacylation of Amide Intermediate #3 as follows. Concentrated hydrogen chloride solution (37.5 w/% in water, five to six-fold molar excess) was added to a solution of one equivalent of Amide Intermediate #3 in ethanol at 0 °C. The reaction mixture was allowed to warm to 10 ambient temperature while being stirred. After the initial foam formation ceased the reaction mixture was stirred at 70 °C for 5 hours. The progress of the reaction was monitored via Gas Chromatography. The Fluorinated Amine Salt #1 was isolated in quantitative yield by stripping all volatiles under reduced pressure.

15 ¹H-NMR (MeOH-d4): 2.39 (m, 2H, CF₂CH₂), 2.81 (m, 4H, CH₂S), 2.90 (m, 2H, SCH₂), 3.05 (m, 2H, and CF₂CH₂CF₂), 3.19 (m, 2H, CH₂N).

Example 9

According to DE10108543(C1), Fluorinated Isocyanate #1 was 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-(2-isocyanato-ethylsulfanyl)-20 octane which was made as follows. A solution of one equivalent of Fluorinated Amine #1 (0.1 mol) and one equivalent of triethyl amine (0.1 mol) in dry toluene (350 mL) is cooled to 0 °C (ice bath). Ethyl chloroformate (0.11 mol) is added dropwise within 20 min. The mixture, while stirring, was allowed to warm to room temperature. A second 25 equivalent of triethyl amine (0.1 mol) is added followed by the dropwise addition of methyl trichlorosilane (0.12 mol) at 30 – 40 °C (addition time about 20-30 min). The mixture was then heated to 100 °C for 1 hour. After the mixture had cooled to ambient temperature the precipitated ammonium salts were filtered off. Under steady N₂ flow, both toluene and 30 generated ethoxy methyl dichlorosilane were distilled off at 200 mm Hg. The residue was dried in vacuum to furnish Fluorinated Isocyanate #1 in

95 % yield as a light red-brown liquid. NMR analysis yielded the following results.

5 $^1\text{H-NMR}$ (CDCl_3): 2.34 (m, 2H, CF_2CH_2), 2.73 (m, 4H, CH_2SCH_2), 3.45 (m, 2H, CH_2N).

13C-NMR (CDCl_3): 23.1 (s, CH_2S), 32.1 (m, CF_2CH_2), 35.8 (s, $\text{SCH}_2\text{CH}_2\text{N}$), 40.5 (s, CH_2N), 106 – 121 (m, CF_2), 123.8 (s, NCO).

Example 10

According to *J. Org. Chem.* **1956**, 21, 404 – 405, Fluorinated Isothiocyanate #1 was 1,1,1,2,2,3,3,4,4,5,5,6,6-tidecafluoro-8-(2-isothiocyanato-ethylsulfanyl)-octane which was made as follows. A solution of one equivalent of Fluorinated Amine #1 (0.1 mol) and two equivalents of triethyl amine (0.2 mol) in dry methylene chloride (200 mL) was cooled to 0°C (ice bath). Carbon disulfide (1.3 equivalents) was added drop-wise within 20 min. The mixture was allowed to warm to ambient temperature while stirring was continued for one hour. The reaction mixture was stirred for additional 8 hours at ambient temperature. Toluene (200 mL) was added and precipitated solids were filtered of (Buechner). The solvents of the filtrate were removed in vacuum to furnish the desired product in sufficient purity for further derivatization in 97% yield. NMR analysis yielded the following results.

1H-NMR (CDCl_3): 2.35 (m, 2H, CF_2CH_2), 2.78 (m, 4H, CH_2SCH_2), 3.68 (m, 2H, CH_2N).

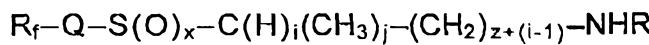
25 13C-NMR (CDCl_3): 23.1 (s, CH_2S), 32.1 (m, CF_2CH_2), 32.6 (s, $\text{SCH}_2\text{CH}_2\text{N}$), 45.0 (s, CH_2N), 106 – 121 (m, CF_2), 133.4 (s, NCO).

09 May 2013

2008334034

The Claims defining the invention are as follows:

1. A fluoroalkyl amine represented by the formula:



wherein:

R_f is chosen from:

- a) $(CF_3)_2CF$;
- b) $(CF_3)_2CH$, $CF_3(CF_2)_2OCFHCF_2$ or HC_mF_{2m} wherein m is 2 to 12;
- c) $CF_3(CF_2)_2OCF_2CF_2$, $CF_3(CF_2)_2OCFHCF_2$ or $CF_3CF_2CF_2[OCF(CF_3)CF_2]_mOCR^1F$ wherein m is an integer from 6 to 15 and R^1 is F, CF_3 or H;
- d) $CF_3(CF_2)_5(CH_2CF_2)_m$ wherein m is 1, 2 or 3; and
- e) $F[(CF_2CF_2)_n(CH_2CH_2)_m]_kCF_2CF_2$ wherein $n = 1, 2$ or 3; $m = 1$ or 2; and $k = 1, 2$ or 3;

Q is chosen from the group consisting of a C_2-C_{12} hydrocarbylene;

x is 1 or 2;

z is 0 or 1;

i is 1 or 2;

j is 0 or 1; provided that $i + j = 2$; and

R is chosen from H and a C_1 to C_4 alkyl.

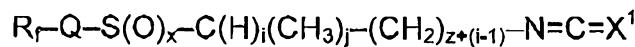
2. The fluoroalkyl amine of claim 1 wherein R is H.

3. The fluoroalkyl amine of claim 1 or claim 2 wherein $i = 1$, $j = 1$ and $z = 0$.

4. The fluoroalkyl amine of claim 1 or claim 2 wherein $i = 2$, $j = 0$ and $z = 0$.

5. A fluoroalkyl isocyanate or isothiocyanate represented by the

formula:



wherein:

X^1 is O or S;

09 May 2013

2008334034

R_f is chosen from

- a) $(CF_3)_2CF$;
- b) $(CF_3)_2CH$, $CF_3(CF_2)_2OCFHCFC_2$ or HC_mF_{2m} wherein m is 2 to 12;
- c) $CF_3(CF_2)_2OCF_2CF_2$, $CF_3(CF_2)_2OCFHCFC_2$ or $CF_3CF_2CF_2[OCF(CF_3)CF_2]_mOCR^1F$ wherein m is an integer from 6 to 15 and R^1 is F, CF_3 or H;
- d) $CF_3(CF_2)_5(CH_2CF_2)_m$ wherein m is 1, 2 or 3; and
- e) $F[(CF_2CF_2)_n(CH_2CH_2)_m]_kCF_2CF_2$ wherein n = 1, 2 or 3; m = 1 or 2; and k = 1, 2 or 3;

Q is chosen from the group consisting of a C_2 – C_{12} hydrocarbylene;

x is 1 or 2;

z is 0 or 1;

i is 1 or 2;

j is 0 or 1; provided that $i + j = 2$.

6. The fluoroalkyl isocyanate or isothiocyanate of claim 5 wherein i = 1, j = 1 and z = 0.

7. The fluoroalkyl isocyanate or isothiocyanate of claim 5 wherein i = 2, j = 0 and z = 0.

8. A method for making a sulfur containing fluoroalkyl amine comprising the steps of:

- a) reacting a thiol represented by R_f-Q-SH with a *N*-vinylamide represented by $H_2C=CH-(CH_2)_y-NR-C(O)-R$ to produce an amide intermediate represented by $R_f-Q-S-C(H)_i(CH_3)_j-(CH_2)_{z+(i-1)}-NR-C(O)-R$ wherein:

R_f is chosen from

- A) $(CF_3)_2CF$;
- B) $(CF_3)_2CH$, $CF_3(CF_2)_2OCFHCFC_2$ or HC_mF_{2m} wherein m is 2 to 12;
- C) $CF_3(CF_2)_2OCF_2CF_2$, $CF_3(CF_2)_2OCFHCFC_2$ or $CF_3CF_2CF_2[OCF(CF_3)CF_2]_mOCR^1F$ wherein m is an integer from 6 to 15 and R^1 is F, CF_3 or H;
- D) $CF_3(CF_2)_5(CH_2CF_2)_m$ wherein m is 1, 2 or 3; and

25

30

2008334034 09 May 2013

E) $F[(CF_2CF_2)_n(CH_2CH_2)_m]_kCF_2CF_2$ wherein $n = 1$,
 2 or 3 ; $m = 1$ or 2 ; and $k = 1$, 2 or 3 ;
each R is independently chosen from H or a C_1 to C_4 alkyl; y
is an integer chosen from 0 to 16 ;
 z is 0 or 1 ;
 i is 1 or 2 , j is 0 or 1 ; provided that $i + j = 2$;

b) optionally reacting the amide intermediate with an oxidizing agent to produce a sulfur oxide intermediate represented by $R_f-Q-S(O)_x-C(H)_i(CH_3)_j-(CH_2)_{z+(i-1)}-NR-C(O)-R$ wherein x is 1 or 2 ;

c) subjecting the amide intermediate or the sulfur oxide intermediate to deacylation to produce the sulfur containing fluoroalkyl amine.

9. The method of claim 8 wherein the deacylation is conducted by:
i) reacting the amide intermediate with a base or
ii) reacting the amide intermediate with an acid or
iii) reacting the amide sulfoxide intermediate with an acid.

10. The method of claim 8 or claim 9 wherein $i = 1$, $j = 1$ and $z = 1$.

11. The method of claim 8 or claim 9 wherein $i = 2$, $j = 0$ and $z = 0$.

12. The fluoroalkyl amine of any one of claims 1 to 4 substantially as hereinbefore described with reference to the accompanying Examples.

13. The fluoroalkyl isocyanate or isothiocyanate of any one of claims 5 to 7 substantially as hereinbefore described with reference to the accompanying Examples.

14. The method of any one of claims 8 to 11 substantially as hereinbefore described with reference to the accompanying Examples.

25