United States Patent Office

3,088,849
Patented May 7, 1963

3,088,849

FLUOROCARBON-SUBSTITUTED MERCAPTANS

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No Drawing. Filed Dec. 11, 1961, Ser. No. 158,608
22 Claims. (Cl. 117—127)

This invention relates to novel and useful fluorocarbon substituted alkyl mercaptans and to a process for their preparation.

It is an object of the present invention to provide certain new fluorocarbon-substituted alkyl mercaptans. It is another object of the present invention to provide compositions of matter which are useful in forming relatively permanent protective surface coatings. It is a further object of the present invention to provide a process by which these products may be produced. Additional objects will be apparent to those skilled in the art from the specifications which follow.

The fluorocarbon-substituted alkyl mercaptans of the present invention can be represented by the formula:

$$R_f—R—SH$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fully fluorinated carbon atoms and —R— is a bridging radical having from 3 to 15 carbon atoms selected from the group consisting of:

$$—(CH_2)_nCH_2—$$

$$—CH_2CHCl(CH_2)_mCH_2—$$

$$—O(CF_2)_2CH_2—$$

$$—\overset{O}{\overset{\|}{C}}—\overset{H}{\overset{|}{N}}—(CH_2)_p—CH_2—$$

and

$$—SO_2—\overset{R'}{\overset{|}{N}}—(CH_2)_p—CH_2—$$

wherein R_f is a perfluoroalkyl group, n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms.

The complete perfluorocarbon structure or group R_f can be a perfluoroalkyl group having an open (acyclic) straight- or branched-chain, or a cyclic structure (e.g. a perfluorocyclohexyl group having a six-membered ring structure) or it can consist of a combination of perfluoroalkyl straight-chain and perfluorocyclic groups. The perfluorocarbon group R_f may be bonded to the alkylene group through either a cyclic or an acyclic carbon atom (that is, this carbon atom may or may not be in a ring) and two carbon atoms of the fluorocarbon group may be linked together by an oxygen atom or three carbons may be linked together by a nitrogen atom, since oxygen and nitrogen provide very stable linkages between fluorocarbon groups and do not interfere with the highly stable and inert character of the complete fluorocarbon group or structure, as is shown, for instance, in U.S. Patent Nos. 2,500,388 and 2,616,927.

The stable and inert terminal perfluorocarbon "tail" is non-polar and is repellent not only to water but also to oils and hydrocarbons. It appears to impart to the compounds of the invention unique surface treatment properties not possessed by corresponding hydrocarbon compounds, the latter being oleophilic and highly soluble in oils and hydrocarbons. When metallic surfaces are coated with the compounds of the invention, the coatings impart oil resistance, water resistance and corrosion resistance to the material coated.

It appears to be required that the perfluorocarbon "tail" contain at least 4 carbon atoms, and the preferred number of carbon atoms is 6 to 10. A terminal fluorocarbon chain of the minimum length insolubilizes the perfluorocarbon end of the molecule and renders it both hydrophobic and oleophobic. Increasing the length of this "tail" decreases solubility still further and enhances the degree of water and oil repellency imparted to surfaces coated with the present compounds. Preferred compounds are the straight-chain mercaptans

$$R_f(CH_2)_nCH_2SH$$

Another very useful group which is especially readily prepared is the group $R_fSO_2NR'(CH_2)_pCH_2SH$. In the formulae R, R_f, R′, p and n have the significance set forth hereinabove.

The length of the divalent linking group represented by —R— in the fluorocarbon-substituted alkyl mercaptan formula, which links the fluorocarbon group to the mercaptan functional group, can be varied, and thereby modifies the physical properties of the compounds such as melting point and flexibility. Thus, the general molecular structure of the present mercaptan compounds can be varied as set forth more specifically hereinafter.

Broadly speaking, the compounds of the present invention can be prepared by interreacting a distally-fluorocarbon substituted alkanol and a hydrogen halide of molecular weight between about 35 and 130 to form the corresponding fluorocarbon-substituted alkyl halide, adding this alkyl halide to thiourea to form the corresponding fluorocarbon-substituted isothiouronium halide, and interreacting the isothiouronium halide with an alkali, such as an alkali metal hydroxide, to form the fluorocarbon alkylene mercaptan. These reactions are represented by the following equations:

$$R_f—R—OH + HX \rightarrow R_f—R—X + HOH$$

$$R_f—R—X + S{=}C(NH_2)_2 \longrightarrow \left[R_f—R—S—C(NH_2)_2\right]^+ X^-$$

$$\left[R_f—R—S—C(NH_2)_2\right]^+ X^- + MOH \longrightarrow$$

$$R_f—R—SH + MX + H_2O + \frac{1}{q}(H_2NCN)_q$$

wherein R_f and R are as previously defined, M is an alkali metal and $(H_2NCN)_q$ is a polymer of cyanamide.

The intermediate fluorocarbon-substituted alkylene isothiouronium halides are stable and can be isolated if desired, but it is often preferable to proceed directly to the next step in the process without isolating the particular intermediate.

It is preferred to use hydrogen bromide in the process of the invention because of the relative ease of reaction. It is also possible, however, to use the other hydrogen halides of molecular weight between about 35 and 130 (i.e. hydrogen iodide and hydrogen chloride). If one of these other reagents is used in place of hydrogen bromide, the corresponding fluorocarbon-substituted alkyl halide and fluorocarbon-substituted isothiouronium halide will be formed. Thus, for example, in the process of the invention 3-(perfluorooctyl)propan-1-ol can be condensed with hydrogen chloride to yield 3-(perfluorooctyl)propyl chloride and the latter can be reacted with thiourea to yield 3-(perfluorooctyl)propyl isothiouronium chloride. Similary if the starting compounds are 11-(perfluorooctyl)undecan-1-ol and hydrogen iodide, 11-(perfluorooctyl)undecyl iodide and 11-(perfluorooctyl)-undecyl isothiouronium iodide will be formed in the process of the invention.

The steps of the process for preparing the fluorocarbon-substituted alkyl mercaptans from the corresponding distally-fluorocarbon-substituted alkanols are carried out at moderate temperatures, generally from about 50° C. to 200° C. Because of the ease of temperature control and reasonable speed of reaction encountered, it is often most convenient to carry out the reactions at reflux. While they may be run below 50° C., this is not ordinarily economically practical. At higher temperatures, the reaction is more difficult to control and undesirable by-products may be formed. The temperatures selected for use in the process tend to affect the length of time required for completion of the reactions, according to the inverse relationship between temperature and duration of reaction commonly encountered in chemical processes.

Moderate pressures are generally satisfactory for the process of the invention, atmospheric pressure being preferred because of its convenience. It might, however, be desirable in some cases to carry out the reaction between the distally-fluorocarbon-substituted alkanol and the hydrogen halide in a pressure vessel at increased pressure in order to reduce the time of reaction. Conventional glass, glass-lined or stainless steel vessels are suitable for carrying out the process of the invention.

Certain of the distally fluorocarbon-substituted alkanol starting compounds for the process of the present invention wherein R is a $-(CH_2)_nCH_2-$ group, can be prepared by reductive dehydrohalogenation of halogenated fluorocarbon-substituted alkanols and produced by desulfonylative addition of fluorocarbonsulfonyl chlorides to unsaturated alkanols, such as allyl alcohol and homologs thereof, followed by reduction, as described in U.S. Patents Nos. 2,951,051 and 2,965,659 and shown in the following equations.

$$R_fSO_2Cl + CH_2{=}CH{-}(CH_2)_m{-}CH_2OH \xrightarrow[\text{initiation}]{\text{free radical}}$$

$$R_fCH_2{-}CHCl{-}(CH_2)_m{-}CH_2OH \xrightarrow[H_2,\ NaOH]{\text{Raney nickel}}$$

$$R_f{-}(CH_2)_n{-}CH_2OH$$

It will be readily apparent that the starting alcohols wherein —R— is a $-CH_2CHCl-(CH_2)_m-CH_2-$ group are available as intermediates in the above preparation when perfluoroalkane sulfonyl chlorides are added to omega-unsaturated alcohols.

Suitable perfluorocarbon-substituted alkanols for use in preparing the mercaptans of the invention are exemplified by 3-(perfluorododecyl)propan-1-ol, 12-(perfluorobutyl)dodecan-1-ol, 11-(perfluorooctyl)undecan-1-ol, 12-(perfluorododecyl)dodecan-1-ol, 3-(perfluorotetradecyl)propan-1-ol, 4-(perfluorooctyl)butan-1-ol, 2-chloro-3-(perfluorooctyl)propan-1-ol, 2-chloro-3-(perfluorododecyl)-propan-1-ol, 2-chloro-3-(perfluorotetradecyl)-propan-1-ol, 3-chloro-4-(perfluorooctyl)butan-1-ol, 11-chloro-12-(perfluorobutyl)-dodecan-1-ol, 10-chloro-β-11-(perfluoro-

octyl)-undecan-1-ol, 11-chloro-12-(perfluoro-dodecyl)-dodecan-1-ol, and the like available by the processes of U.S. Patents Nos. 2,951,051 and 2,965,659; 1,1-dihydro-4-oxaperfluorooctanol-1, 1,1-dihydro-4-oxaperfluoro dodecanol-1, 1,1-dihydro-4-oxaperfluorononanol-1 and the like prepared by reduction of the acids of U.S. Patent No. 2,713,593 with lithium aluminum hydride as described therein; N-perfluorocapryloyl ethanolamine, N-perfluoro valeroyl ethanolamine, N-perfluorododecanoyl-7-amino-heptanol-1, N-perfluorooctanoyl-3-amino-propanol-1 and the like prepared by aminolysis of an ester of the perfluorinated carboxylic acid with the amino alcohol as described in U.S. Patent 2,764,602; 2-(N-methyl perfluorooctanesulfonamido)-ethanol, 11-(N-ethyl perfluorobutanesulfonamido)-undecanol-1, 5-(N-propyl perfluorododecane-sulfonamido) - pentanol-1, 2-(N-propyl perfluorooctanesulfonamido)ethanol and the like described in U.S. Patent No. 2,803,656.

The mercaptans of the invention range in physical properties from high boiling liquids to solids, as the chain length increases. They are stable and lower members of the series can be distilled under reduced pressure. They are insoluble in water and only slightly soluble in the ordinary organic solvents, but are more soluble in fluorinated organic solvents.

Having now generally described the processes employed in making the compounds of the invention I now provide several examples illustrating in greater detail processes and compositions of the invention. It should be understood, however, that this is done solely by way of example of the best mode contemplated for practicing the invention, and is intended neither to delineate the scope of the invention nor to limit the ambit of the appended claims. In these examples where not otherwise specified parts are by weight and temperatures in degrees centigrade.

Example 1

A mixture of 68 g. (0.142 mole) of 3-(perfluorooctyl) propan-1-ol, 61.5 g. of 48 percent hydrobromic acid, 15.7 g. of concentrated sulfuric acid and 125 ml. of toluene is refluxed for 8 hours. The mixture is then neutralized with aqueous sodium carbonate solution; the emulsion which forms is broken by the addition of ether. The ether-toluene layer is separated and the solvents are removed by distillation. The viscous material which remains after the solvents are removed is flash distilled and the residue is crude 3-(perfluorooctyl)-propyl bromide. Without further purification, the bromide is dissolved in 50 ml. of ethanol. One hundred ml. of ethanol containing 10.7 g. of dissolved thiourea are added and the mixture is refluxed for approximately 7 hours. One hundred ml. of petroleum ether are then added to the reaction mixture and 3-(perfluorooctyl)propyl isothiouronium bromide formed in the reaction separates as a precipitate. This product is removed by filtration and air dried. The salt is then hydroylzed by heating with 100 ml. of 10 percent aqueous sodium hydroxide solution for ½ hour on a steam bath and the mixture is neutralized with dilute hydrochloric acid and extracted with ether. The solvent is removed from the ether solution and aproximately 10 g. of a liquid identified as crude 3-(perfluorooctyl)propyl mercaptan remain. This crude product is distilled and 8.5 g. of the purified product, B.P. 60–66° C. at 0.75 mm. of mercury pressure having a refractive index $n_D^{25}=1.3380$, are recovered. The infrared spectral absorption analysis is consistent with the structure,

$$C_8F_{17}(CH_2)_3SH$$

and analysis shows 6.0 percent of sulfur as compared to a calculated value of 6.49 percent.

Example 2

About 50 g. of 11-(perfluorooctyl)undecan-1-ol are placed in a flask and heated to approximately 95° C. on a steam bath. A total of 0.45 mole of hydrogen bromide

gas is bubbled through the hot melt. The resulting dark colored mixture is shaken with an equal volume of concentrated sulfuric acid and heptane is added to assist in phase separation. The sulfuric acid layer is separated and the heptane layer is washed with 50 percent aqueous methanol and sufficient aqueous ammonium hydroxide is added to bring the mixture to a pH of approximately 9. The resulting emulsion is broken when a small amount of saturated aqueous potassium chloride solution is added. The heptane layer is then separated and dried over magnesium sulfate. The solvent is removed from the heptane solution and approximately 41.1 g. (a 75 percent yield) of a low melting waxy solid identified as 11-(perfluorooctyl) undecyl bromide remain. The boiling point of this material is 108–112/0.1 mm. and has refractive index $n_D^{25}=1.3815$.

Analysis shows the presence of 35.3 percent of carbon, 49.6 percent of fluorine and 12.4 percent of bromine as compared to calculated values of 34.9 percent, 49.5 percent and 12.2 percent respectively.

A mixture of 6.67 g. (0.01 mole) of 11-(perfluorooctyl)-undecyl bromide and 0.76 g. (0.01 mole) of thiourea in 25 milliliters of 95 percent ethanol is refluxed with stirring for 64 hours during which time the fluorocarbon-substituted alkyl bromide and the thiourea react to form 11-(perfluorooctyl)undecylisothiouronium bromide. A solution of 0.06 g. of sodium hydroxide in 20 ml. of water is then added and this mixture is stirred and refluxed for 3 hours. On cooling, a two-phase mixture forms, of which the lower phase solidifies. The solid product consisting of the 11-(perfluorooctyl)undecylmercaptan formed in the reaction is removed by filtration and is dried. Its melting point is 40–42° C. The product is purified by recrystallization from ethanol and sublimation. The 11-(perfluorooctyl)undecylmercaptan thus purified melts at about 44–46° C., and is found to contain 37.8 percent of carbon and 5.12 percent of sulfur as compared to the theoretical values of 37.6 percent and 5.28 percent respectively.

5 - (perfluorooctyl)pentylmercaptan, 12 - (perfluorobutyl) - dodecylmercaptan and 3 - (perfluorododecyl) propylmercaptan are prepared by repeating the processes of Examples 1 and 2 except that 5-(perfluorooctyl) pentan-1-ol, 12-(perfluorobutyl)dodecan-1-ol and 3-(perfluorododecyl)propan-1-ol are respectively used as starting materials.

Example 3

Clean copper strips are dipped into a saturated solution of 11-(perfluorooctyl)undecyl mercaptan in methanol (of the order of 1%), drained and the remaining solvent is allowed to evaporate. The copper is not noticeably discolored nor is there any other apparent change in the surface of the metal. The amount of the mercaptan coated on the metal is so small that it is not measurable by ordinary techniques. When it is wet with water or with oily materials, however, there is a "beading up" of the liquids on the metal surface indicating that no wetting is taking place (in contrast to the uncoated metal surface). The metal so coated with the fluorocarbon-substituted-alkane thiol, is protected against corrosion, as is illustrated by dipping the treated strips along with untreated copper control strips in an approximately 2 percent aqueous solution of sodium sulfide. This test simulates the corrosive action of the atmosphere, particularly in industrial areas in which there is a relatively high proportion of such gases as hydrogen sulfide and sulfur dioxide, but at an enormously accelerated rate. The control strips darken immediately upon contact with the solution, but no discoloration or other change is noted on the coated strips after 24 hours.

In another series of tests a 5 percent solution of 11-(perfluorooctyl)undecylmercaptan in a 50 percent benzotrifluoride, 50 percent methyl perfluorobutyrate solvent is coated on a copper surface. Upon evaporation of the solvents the surface appears to have darkened slightly but retains the characteristic copper color and appearance. This surface cannot be wet by water or oily materials, and the metal is resistant to corrosion. Furthermore, the coating is relatively permanently bonded to the surface since it cannot be removed by washing with the solvent system from which it was applied.

In still another series of tests, strips of silver are dipped into a saturated solution of 11-(perfluorooctyl)undecylmercaptan in methanol, drained and the remaining solvent is allowed to evaporate. There is no noticeable discoloration of these strips but the previously mentioned ability to resist wetting by water or oily materials is again noted. These strips are placed along with untreated silver strips in an approximately 2 percent aqueous solution of sodium sulfide. The untreated silver strips are more resistant than copper to attack by the solution but within ½ hour they have discolored. The coated silver strips, however, are unchanged after 24 hours.

When bronze bushings intended for use as bearing inserts are treated as set forth above with the compounds named, they are protected from corrosion during storage and subsequent use.

Example 4

Clean copper strips are dipped into liquid 3-(perfluorooctyl)propylmercaptan and are drained dry. The hydrophobic and oleophobic surface properties mentioned in the previous example are found here also. No change of the metal color is noted. Useful protection is afforded to these strips throughout a 24 hour cycle in an approximately 2 percent aqueous solution of sodium sulfide. Similar protection for various metals is also obtained by coating them with 5-(perfluorooctyl)pentylmercaptan and the other mercapto compounds of the invention.

Example 5

The procedure described hereinabove in Examples 1 and 2 is applicable to other carbinols to form other mercaptans of the invention. In each case the bromide and isothiouronium intermediates are formed and the latter is converted to the mercaptan. The following tabulation shows the mercaptans formed when the above processes are applied to the enumerated carbinols.

Carbinol employed in process	Mercaptan produced
$C_8F_{17}—CH_2—CHCl—CH_2OH$	$C_8F_{17}—CH_2—CHCl—CH_2—SH$
$C_{12}F_{25}—CH_2—CHCl—CH_2OH$	$C_{12}F_{25}—CH_2—CHCl—CH_2—SH$
$C_{14}F_{29}—CH_2—CHCl—CH_2OH$	$C_{14}F_{29}—CH_2—CHCl—CH_2SH$
$C_8F_{17}—CH_2—CHCl—CH_2—CH_2OH$	$C_8F_{17}—CH_2—CHCl—CH_2—CH_2—SH$
$C_4F_9—CH_2—CHCl—(CH_2)_9—CH_2OH$	$C_4F_9—CH_2—CHCl—(CH_2)_9—CH_2—SH$
$C_8F_{17}—CH_2—CHCl—(CH_2)_8—CH_2OH$	$C_8F_{17}—CH_2—CHCl—(CH_2)_8—CH_2—SH$
$C_{12}F_{25}—CH_2—CHCl—(CH_2)_9—CH_2OH$	$C_{12}F_{25}—CH_2—CHCl(CH_2)_9—CH_2SH$
$C_4F_9—O—(CF_2)_2—CH_2OH$	$C_4F_9—O—(CF_2)_2—CH_2—SH$
$C_8F_{17}—O—(CF_2)_2—CH_2OH$	$C_8F_{17}—O—(CF_2)_2—CH_2—SH$
$C_6F_{11}—O—(CF_2)_2—CH_2OH$	$C_6F_{11}—O—(CF_2)_2—CH_2—SH$
$C_8F_{17}SO_2N(CH_3)—CH_2—CH_2OH$	$C_8F_{17}SO_2N(CH_3)—CH_2—CH_2—SH$
$C_4F_9SO_2N(C_2H_5)—(CH_2)_{10}—CH_2OH$	$C_4F_9SO_2N(C_2H_5)—(CH_2)_{10}—CH_2—SH$
$C_8F_{17}SO_2N(C_3H_7)—CH_2—CH_2OH$	$C_8F_{17}SO_2N(C_3H_7)—CH_2—CH_2—SH$
$C_7F_{15}CONHCH_2CH_2OH$	$C_7F_{15}CONHCH_2CH_2SH$
$C_4F_9CONHCH_2CH_2OH$	$C_4F_9CONHCH_2CH_2SH$
$C_{11}F_{23}CONH(CH_2)_7OH$	$C_{11}F_{23}CONH(CH_2)_7SH$
$C_7F_{15}CONH(CH_2)_3OH$	$C_7F_{15}CONH(CH_2)_8SH$

The intermediate bromides and isothiouronium salts produced in the above reactions have the formulae respectively:

Intermediate bromides	Intermediate isothiouronium salts
$C_8F_{17}CH_2CHCl-CH_2Br$	$C_8F_{17}CH_2CHCl-CH_2-S-C(NH_2)=NH_2Br$
$C_{12}F_{25}CH_2CHCl-CH_2Br$	$C_{12}F_{25}CH_2CHCl-CH_2-S-C(NH_2)=NH_2Br$
$C_{14}F_{29}-CH_2-CHCl-CH_2Br$	$C_{14}F_{29}CH_2CHCl-CH_2S-C(NH_2)=NH_2Br$
$C_8F_{17}-CH_2-CHClCH_2-CH_2Br$	$C_8F_{17}-CH_2CHClCH_2CH_2S-C(NH_2)=NH_2Br$
$C_4F_9-CH_2-CHCl(CH_2)_9-CH_2Br$	$C_4F_9-CH_2CHCl-(CH_2)_9-CH_2S-C(NH_2)=NH_2Br$
$C_8F_{17}-CH_2-CHCl(CH_2)_8-CH_2Br$	$C_8F_{17}-CH_2CHCl-(CH_2)_8-CH_2S-C(NH_2)=NH_2Br$
$C_{12}F_{25}-CH_2-CHCl-(CH_2)_{10}Br$	$C_{12}F_{25}-CH_2CHCl-(CH_2)_{10}-S-C(NH_2)=NH_2Br$
$C_4F_9-O-(CF_2)_2-CH_2Br$	$C_4F_9-O-(CF_2)_2-CH_2S-C(NH_2)=NH_2Br$
$C_8F_{17}-O-(CF_2)_2-CH_2Br$	$C_8F_{17}-O-(CF_2)_2-CH_2S-C(NH_2)=NH_2Br$
$C_5F_{11}-O-(CF_2)_2-CH_2Br$	$C_5F_{11}-O-(CF_2)_2-CH_2S-C(NH_2)=NH_2Br$
$C_8F_{17}SO_2N(CH_3)-CH_2-CH_2Br$	$C_8F_{17}SO_2N(CH_3)CH_2-CH_2S-C(NH_2)=NH_2Br$
$C_4F_9SO_2N(C_2H_5)(CH_2)_{11}Br$	$C_4F_9SO_2N(C_2H_5)(CH_2)_{11}S-C(NH_2)=NH_2Br$
$C_{12}F_{25}-SO_2N(C_3H_7)(CH_2)_5Br$	$C_{12}F_{25}SO_2N(C_3H_7)(CH_2)_6S-C(NH_2)=NH_2Br$
$C_8F_{17}SO_2N(C_3H_7)-CH_2-CH_2Br$	$C_8F_{17}SO_2N(C_3H_7)-CH_2-CH_2S-C(NH_2)=NH_2Br$
$C_7F_{15}CONHCH_2CH_2Br$	$C_7F_{15}CONHCH_2CH_2S-C(NH_2)=NH_2Br$
$C_4F_9CONHCH_2CH_2Br$	$C_4F_9CONHCH_2CH_2S-C(NH_2)=NH_2Br$
$C_{11}F_{23}CONH(CH_2)_7Br$	$C_{11}F_{23}CONH(CH_2)_7S-C(NH_2)=NH_2Br$
$C_7F_{15}CONH(CH_2)_3Br$	$C_7F_{15}CONH(CH_2)_3S-C(NH_2)=NH_2Br$

In the above tabulation it will be understood that the group $-C(NH_2)=NH_2Br$ is a linear representation of the group

$$-\overset{NH_2^+}{\overset{\|}{C}}-NH_2\ Br^-$$

When clean copper strips are treated with the above produced mercaptans as described in Example 3, it is found that the copper is significantly protected against the corrosive action of hydrogen sulfide. The surfaces after treatment are not wet by water or oily materials. In the same way silver strips are protected against tarnishing.

The terms and expressions which have been employed are used as terms of description and not of limitation, and it is not intended, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

This application is a continuation-in-part of my copending application Serial Number 724,203, filed March 26, 1958, now abandoned.

What is claimed is:

1. Fluorocarbon-substituted alkyl mercaptans represented by the formula:

$$R_f—R—SH$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms and —R— is an alkylene bridging radical having from 3 to 15 carbon atoms selected from the group consisting of

$$-(CH_2)_nCH_2-$$

$$-CH_2CHCl(CH_2)_mCH_2-$$

$$-O(CF_2)_2CH_2-$$

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_p-CH_2-$$

and

$$-SO_2-\overset{R'}{\overset{|}{N}}-(CH_2)_p-CH_2-$$

wherein n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms.

2. Fluorocarbon substituted alkyl mercaptans of the formula:

$$R_f—alk—SH$$

wherein R_f is a saturated fluorocarbon structure, containing from 4 to 18 fluorinated carbon atoms and —alk— is an alkylene radical having from 3 to 15 carbon atoms.

3. 3-(perfluorooctyl)propylmercaptan.

4. 11-(perfluorooctyl)undecylmercaptan.

5. 5-(perfluorooctyl)pentylmercaptan.

6. Fluorocarbon-substituted alkyl halides represented by the formula:

$$R_f—R—X$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms, —R— is an alkylene bridging radical having from 3 to 15 carbon atoms selected from the group consisting of

$$-(CH_2)_nCH_2-$$

$$-CH_2CHCl(CH_2)_mCH_2-$$

$$-O(CF_2)_2CH_2-$$

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_p-CH_2-$$

and

$$-SO_2-\overset{R'}{\overset{|}{N}}-(CH_2)_p-CH_2-$$

wherein n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms and X is a halogen atom of atomic weight between about 35 and 130.

7. Fluorocarbon-substituted alkyl halides represented by the formula:

$$R_f—alk—X$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms, —alk— is an alkylene radical having from 3 to 15 carbon atoms and X is a halogen atom of atomic weight between about 35 and 130.

8. Fluorocarbon-substituted alkyl bromides represented by the formula:

$$R_f—R—Br$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms and —R— is an alkylene bridging radical having from 3 to 15 carbon atoms selected from the group consisting of

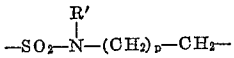
$$-(CH_2)_nCH_2-$$

$$-CH_2CHCl(CH_2)_mCH_2-$$

$$-O(CF_2)_2CH_2-$$

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_p-CH_2-$$

and



wherein n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms.

9. Fluorocarbon-substituted alkyl bromides represented by the formula:

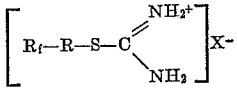
$$R_f—alk—Br$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms and —alk— is an alkylene radical having from 3 to 15 carbon atoms.

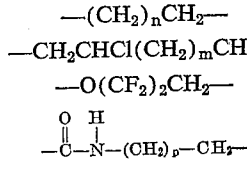
10. 3-(perfluorooctyl)propyl bromide.

11. 11-(perfluorooctyl)undecyl bromide.

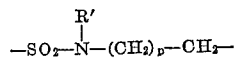
12. Fluorocarbon-substituted isothiouronium halides represented by the formula:



wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms, —R— is an alkylene bridging radical having from 3 to 15 carbon atoms selected from the group consisting of

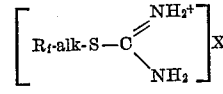


and



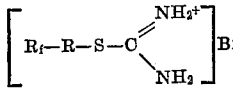
wherein n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms, and X is a halogen atom of atomic weight between about 35 and 130.

13. Fluorocarbon-substituted isothiouronium halides represented by the formula:

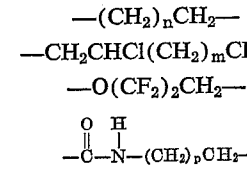


wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms, —alk— is an alkylene radical having from 3 to 15 carbon atoms and X is a halogen atom of atomic weight between about 35 and 130.

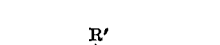
14. Fluorocarbon-substituted isothiouronium bromides represented by the formula:



wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms and —R— is an alkylene bridging radical having from 3 to 15 carbon atoms selected from the group consisting of



and



wherein n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms.

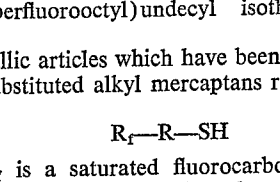
15. 3-(perfluorooctyl)propyl isothiouronium bromide.

16. 11-(perfluorooctyl)undecyl isothiouronium bromide.

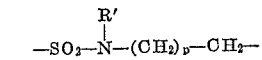
17. Metallic articles which have been coated with fluorocarbon-substituted alkyl mercaptans represented by the formula:

$$R_f—R—SH$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms and —R— is an alkylene bridging radical having from 3 to 15 carbon atoms selected from the group consisting of



and



wherein n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms.

18. Metallic articles which have been coated with fluorocarbon-substituted alkyl mercaptans represented by the formula:

$$R_f—alk—SH$$

wherein R_f is a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms and —alk— is an alkylene radical having from 3 to 15 carbon atoms.

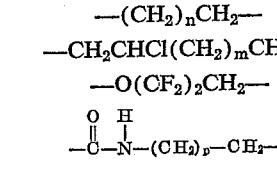
19. Metallic articles which have been coated with 3-(perfluorooctyl)propylmercaptan.

20. Metallic articles which have been coated with 11-(perfluorooctyl)undecylmercaptan.

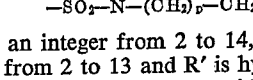
21. The process for the production of fluorocarbon-substituted alkyl mercaptans which comprises condensing a fluorocarbon-substituted alkanol represented by the formula:

$$R_f—R—OH$$

wherein R_f represents a saturated fluorocarbon structure containing from 4 to 18 fluorinated carbon atoms and R represents an alkylene bridging radical having from 3 to 15 carbon atoms, selected from the group consisting of



and



wherein n is an integer from 2 to 14, m is n minus 2, p is an integer from 2 to 13 and R′ is hydrogen or an alkyl group having 1 to 6 carbon atoms, with a hydrogen halide of molecular weight between about 35 and 130 to form the corresponding fluorocarbon-substituted alkyl halide, interreacting the said halide with thiourea to produce the corresponding isothiouronium salt, and hydrolyzing the said isothiouronium salt with alkali.

22. The process according to claim 21 wherein the hydrogen halide is hydrogen bromide.

References Cited in the file of this patent

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