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(54) **Title:** METHOD FOR RECOVERING SULFONIC ESTERS OR SULFONYL HALIDES FROM SALTS OF SULFONIC ACIDS

(57) **Abstract:** A method for the obtainment of an ester or a halide of a fluorinated sulfonic acid from an salt of a sulfonic acid is herein disclosed. The method is particularly useful for recovering waste sulfonate salts from reaction mixtures obtained by reaction of sulfonic esters of alcohols having a pKa lower than 15 with nucleophile compounds.



Description

Method for recovering sulfonic esters or sulfonyl halides from salts of sulfonic acids

Cross-reference to related application

[0001] This application claims priority from European patent application No. 15178203.4, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to a method for the recovery of sulfonic esters or sulfonyl halides, in particular esters or halides of (per)fluoroalkyl sulfonic acids or of (per)fluoro(poly)oxyalkyl sulfonic acids, from salts of sulfonic acids.

Background Art

[0003] Sulfonyl halides are used in organic chemistry for converting certain alcohols, like fluorinated alcohols and phenols, which have a pK_a lower than 15, into the corresponding sulfonic esters, thereby making such alcohols reactive to nucleophilic substitution. For example, **TONELLI, et al.** Linear perfluoropolyether difunctional oligomers: chemistry, properties and applications. *Journal of Fluorine Chemistry*. 1999, vol.95, p.51 - 57. , teach that (per)fluoropolyether (PFPEs) alcohols of the formula R_fCH_2OH (wherein R_f is a perfluoropolyether chain) and having a pK_a of about 12.4 can be conveniently activated to nucleophilic substitution by reaction with perfluorobutanesulfonyl fluoride ($CF_3CF_2CF_2CF_2SO_2F$) to provide the corresponding sulfonic esters $R_fCH_2OSO_2CF_2CF_2CF_2CF_3$ (nonaflate esters), which can be reacted with nucleophile compounds in the presence of a base. At the end of the reaction, beside the desired substitution product, the reaction mixture contains a salt of the sulfonic acid corresponding to the sulfonic halide used. For example, if $CF_3CF_2CF_2CF_2SO_2F$ is used to activate an alcohol and sodium *t*-butoxide is used as base in the nucleophilic substitution reaction, sodium perfluorobutanesulfonate ($CF_3CF_2CF_2CF_2SO_3^-Na^+$) would be obtained as by-product. The sulfonic acid salt (sulfonate salt) is usually separated from the mixture and discarded, which has negative economic impact, especially on an

industrial scale; it would therefore be useful to provide a method avoiding the discharge of the sulfonate salt.

- [0004] **CONTE, et al.** A new method for recovering waste alkaline perfluoro-n-butanesulfonate. *Journal of Fluorine Chemistry*. 1991, vol. 53, p.277-283. , report on a process for the recovery of perfluorobutane sulfonic acid from waste $\text{CF}_3(\text{CF}_2)_3\text{SO}_3\text{-Na}^+$ obtained as product in reactions wherein $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{-OCH}_2\text{CF}_3$ is used as alkylating agent. The authors teach that $\text{CF}_3(\text{CF}_2)_3\text{SO}_3\text{-Na}^+$ can be converted into the corresponding sulfonic acid $\text{CF}_3(\text{CF}_2)_3\text{SO}_3\text{H}$ and that this acid can either be transformed into $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{-OCH}_2\text{CF}_3$ or into $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{Cl}$ or $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{F}$ that is subsequently esterified with $\text{CF}_3\text{CH}_2\text{OH}$. Conte *et al*/further teach to prepare $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{Cl}$ by treatment of $\text{CF}_3(\text{CF}_2)_3\text{SO}_3\text{H}$ with PCl_5 and to convert $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{Cl}$ into $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{F}$ by ion exchange. This method provides $\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{F}$ in fairly good yields (58-74%); however, it employs PCl_5 as key reagent, which is toxic. Moreover, PCl_5 is converted to POCl_3 , which cannot be re-used in a further sulfonate salt conversion reaction because it is not sufficiently reactive.
- [0005] **US 2732398** to Minnesota Mining & Manufacturing Company relates to certain fluorocarbon sulfonic acids and to a process for their manufacture by means of an electrochemical process which leads to "... *the saturated perfluoro sulfonyl compounds, from which the sodium and potassium salts can be made ... and ... converted ... to the perfluoro sulfonic acids*" (col. 5, lines 22 - 26). Example 1 (col. 8, lines 50 - 65) discloses in particular the conversion of $\text{CF}_3\text{SO}_3\text{H}$ into $\text{CF}_3\text{SO}_3\text{Cl}$ by treatment with PCl_5 . Therefore, this method suffers from the same disadvantages as those affecting the method disclosed in the above-discussed article of Conte *et al*.
- [0006] **SCOTT, et al.** A general method for the preparation of perfluoroalkanesulfonyl chlorides. *Journal of Fluorine Chemistry*. 2005, vol.126, p.1196 - 1201. , teach to prepare a perfluoroalkylsulfonyl chloride through a two-step one-pot synthesis comprising the reaction of a iodoperfluoroalkane with sodium dithionite to provide a sodium perfluoroalkyl sulfinatate salt which is subsequently oxidized with

N-chlorosuccinimide. This document does not provide any hint or suggestion to the conversion of an alkaline perfluoroalkyl sulfonyl salt into the corresponding halide.

[0007] The need is thus still felt for an industrially applicable method for the conversion of salts of sulfonic acids into sulfonyl derivatives that can be conveniently used as sulfonating agent, said method avoiding the use of toxic reagents and providing high yields.

Summary of invention

[0008] The Applicant has surprisingly found out that salts of fluorinated sulfonic acids can be easily converted into corresponding phenolic esters by treatment with a phenol that bears at least one electron-withdrawing group and that the phenolic esters can in turn be converted into sulfonyl halides by treatment with an anhydrous alkali- or alkali-earth metal halide. Either the phenolic esters or the sulfonyl halides can be used as sulfonating agents, in particular as sulfonating agents for fluorinated and aromatic alcohols having a pK_a lower than 15.

[0009] Accordingly, the present invention relates to a method [method (M-1)] for the obtainment of an ester or a halide of a fluorinated sulfonic acid from an salt of a sulfonic acid, said process comprising the following steps:

- a) reacting a salt of a fluorinated sulfonic acid [salt (S)] with a strong mineral acid [acid (A_M)] to provide the corresponding fluorinated sulfonic acid [acid (A_S)];
- b) reacting the fluorinated sulfonic acid (A_S) from step a) with a phenol substituted with at least one electron-withdrawing group to provide the corresponding ester of sulfonic acid (A_S) [sulfonic ester (E_S)]; and, optionally
- c) reacting ester (E_S) with an anhydrous alkali- or alkali-earth metal halide to provide the corresponding fluorinated sulfonyl halide [sulfonyl halide (A_{SH})].

[0010] In a preferred aspect, the invention relates to a method [method (M-2)] which comprises using method (M-1) to obtain sulfonic esters (E_S) or sulfonyl halides (A_{SH}) from waste sulfonic acids salts (S), i.e. salts (S) separated from reaction mixtures containing salts (S) as by-products.

[0011] In a further preferred aspect, the invention relates to a method [method (M-3)] for the manufacture of a sulfonic ester of a fluorinated or aromatic alcohol, in particular of a (per)fluoropolyether (PFPE) alcohol, said method comprising obtaining an ester (E_S) or a sulfonyl halide (A_{SH}) as defined above according to method (M-1) or (M-2) and then reacting said ester or halide with a fluorinated or aromatic alcohol.

General definitions, symbols and abbreviations

- [0012] For the avoidance of doubt, throughout the present application, the expression “fluorinated sulfonic acid” denotes a (per)fluoroalkyl sulfonic acid or a (per)fluoro(poly)oxyalkyl sulfonic acid.
- [0013] A (per)fluoroalkyl sulfonic acid is a fully or partially fluorinated alkyl sulfonic acid, while a (per)fluoro(poly)oxyalkyl sulfonic acid is a fully or partially fluorinated alkyl sulfonic acid comprising one or more ethereal oxygen atoms in the alkyl chain.
- [0014] The acronym “PFPE” stands for “(per)fluoropolyether”, i.e. fully or partially fluorinated polyether. When this acronym is used as substantive in the plural form, it is referred to as “PFPEs”.
- [0015] The term “(per)haloalkyl” denotes a straight or branched alkyl group wherein one or more hydrogen atoms have been replaced with halogen atoms.
- [0016] Unless otherwise indicated, the term “halogen” includes fluorine, chlorine, bromine or iodine.
- [0017] The use of parentheses “(…)” before and after names, symbols or numbers identifying formulae or parts of formulae like, for example “formula (S)”, “chain (R_f)” has the mere purpose of better distinguishing those names, symbols or numbers from the rest of the text; thus, said parentheses could also be omitted.
- [0018] The adjective “aromatic” denotes any cyclic moiety having a number of π electrons equal to $4n+2$, wherein n is 0 or any positive integer.
- [0019] The expression “average functionality (F)” denotes the average number of functional groups per polymer molecule and can be calculated according to methods known in the art. For example, the average functionality (F) of PFPE alcohols can be calculated following the method reported in EP

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[0020] When ranges are indicated, range ends are included.

[0021] The expression “as defined above” is intended to comprise all generic and specific or preferred definitions referred to by that expression in preceding parts of the description, unless indicated otherwise.

Detailed description of the invention

Method (M-1) – step a)

[0022] The method of the present invention can be applied both to inorganic and organic salts of sulfonic acids. In other words, the method can be used to obtain sulfonic esters (E_S) and sulfonyl halides (A_{SH}) from inorganic and organic salts of sulfonic acids.

[0023] For the purpose of the present description, inorganic salts are alkali- or alkali-earth metal (i. e. a metal belonging to Group I or Group II of the periodic table) salts of sulfonic acids, preferably alkali metal salts, while organic salts are ammonium and phosphonium salts. Examples of ammonium salts are those formed by reaction of a sulfonic acid with a tertiary amine, while examples of phosphonium salts are those formed by reaction of a sulfonic acid with a trialkylphosphine. Preferred examples of ammonium salts are those formed by reaction of a sulfonic acid with a tertiary amine selected from trimethylamine, triethylamine and tributylamine. Preferred examples of phosphonium salts are those formed by reaction of a sulfonic acid with trimethylphosphine, triethylphosphine and tributylphosphine.

[0024] According to a preferred embodiment, the alkali salt of fluorinated sulfonic acid [salt (S)] used in step a) of method (M-1) is an alkali metal salt complying with formula:

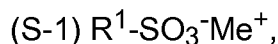


wherein:

- R is a (per)fluoroalkyl or a (per)fluoro(poly)oxyalkyl chain comprising a -CF₂- group directly bound to the sulphur atom of the -SO₃⁻ group and
- Me⁺ is an alkali metal cation, preferably a sodium or potassium cation.

[0025] In a first aspect, the salt (S) is an alkali metal salt of a (per)fluoroalkyl sulfonic acid [salt (S-1)].

[0026] Typically, salt (S-1) complies with formula:



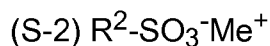
wherein:

- R^1 is a C_1 - C_{10} (per)fluoroalkyl chain, i.e. a straight or branched fully or partially fluorinated C_1 - C_{10} alkyl chain, preferably a straight or branched C_1 - C_4 (per)fluoroalkyl chain, with the proviso that chain R^1 contains a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group. More preferably, chain R^1 is a perfluoroalkyl chain, still more preferably a straight perfluoroalkyl chain, even more preferably a straight C_1 - C_4 perfluoroalkyl chain; and
- Me^+ is an alkali metal cation, preferably a sodium or potassium cation.

[0027] Preferred examples of salts (S-1) are sodium and potassium trifluoromethanesulfonate (triflate), sodium and potassium pentafluoroethane sulfonate, sodium and potassium heptafluoropropanesulfonate and sodium and potassium nonafluorobutanesulfonate (nonaflate), sodium and potassium nonaflate being preferred.

[0028] In a second aspect, the salt (S) is an alkali metal salt of a (per)fluoro(poly)oxyalkyl sulfonic acid [salt (S-2)].

[0029] Typically, salt (S-2) complies with formula:



wherein:

- R^2 is a straight or branched C_1 - C_{10} (per)fluoro(poly)oxyalkyl chain, i.e. a straight or branched fully or partially fluorinated C_1 - C_{10} alkyl chain comprising one or more ethereal oxygen atoms, preferably a straight or branched C_1 - C_4 (per)fluoro(poly)oxyalkyl chain, with the proviso that chain R^2 contains a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group. More preferably, chain R^2 is a perfluoro(poly)oxyalkyl chain, even more preferably a straight perfluoro(poly)oxyalkyl chain, still more preferably a straight C_1 - C_4 perfluoro(poly)oxyalkyl chain; and
- Me^+ is an alkali metal cation, preferably a sodium or potassium cation.

[0030] A preferred example of salt (S-2) is $C_2F_5OCF_2CF_2SO_3^- K^+$ (potassium perfluoro(2-ethoxyethane)sulfonate).

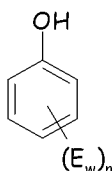
- [0031] Preferably, salts (S) is a salt (S-1).
- [0032] The strong mineral acid [acid (A_M)] used in step a) is an inorganic acid having a pK_a lower than 0, preferably lower than -3. Preferred examples of acids (A_M) are fluorosulfonic and sulphuric acid; still more preferably, acid (A_M) is sulphuric acid. It is preferred that acid (A_M) is anhydrous.
- [0033] An excess of acid (A_M) with respect to salt (S) is typically used in step a). Preferably, acid (A_M) is used in an equivalent ratio ranging from 2 to 5 with respect to salt (S).
- [0034] Step a) is generally carried out by adding salt (S) to acid (A_M) to obtain a mixture that is heated at a temperature of at least 10°C, preferably ranging from 10°C to 100°C, more preferably from 20°C to 50°C, for a time typically ranging from 1 to 4 hours. A person skilled in the art will be able to determine the reaction temperature and time according to known methods on a case-by-case basis according to the selected salt (S) and acid (A_M). In any case, the completion of the reaction can be followed withdrawing a sample and submitting the sample to ^{19}F -NMR analysis. The reaction is complete when shifts from -114.3 ppm ($-\text{CF}_2\text{SO}_3\text{M}$ signal) to -112 ($-\text{CF}_2\text{SO}_3\text{H}$ signal) and from -121 ppm ($-\text{CF}_2\text{-CF}_2\text{SO}_3\text{M}$ signal) to -122 ($-\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ signal) are observed.
- [0035] The resulting fluorinated sulfonic acid (S_A) is recovered from the reaction mixture according to methods known in the art, typically distillation which can be determined by the person skilled in the art on a case-by-case basis.
- [0036] If a salt (S-1) is used as starting material, step a) leads to a (per)fluoroalkyl sulfonic acid (S_{A-1}) complying with formula:
(S_{A-1}) $\text{R}^1\text{-SO}_3\text{H}$
wherein R^1 is as defined above.
- [0037] If a salt (S-2) is used as starting material, step a) leads to a (per)fluoro(poly)oxyalkyl sulfonic acid (S_{A-2}) complying with formula:
(S_{A-2}) $\text{R}^2\text{-SO}_3\text{H}$
wherein R^2 is as defined above.

Method (M-1) – step b)

- [0038] In step b), the sulfonic acid (S_A) obtained from step a) is reacted with a

phenol [phenol (W_p) substituted with at least one electron-withdrawing group, herein after identified with the symbol (W_p). "At least one" means that the phenol can contain from 1 to 5 electron-withdrawing groups. For the purposes of the present invention, the at least one electron-withdrawing group is typically selected from one or more of nitro, cyano, perfluoro alkyl, typically C_1 - C_3 perfluoroalkyl, and fluorine. More preferably phenol (W_p) comprises at least one nitro- or cyano- group. Still more preferably, the phenol is 4-nitrophenol or 4-cyanophenol.

[0039] Phenol (W_p) can thus be represented with the formula here below:



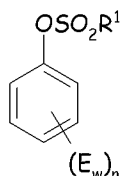
wherein E_w is an electron-withdrawing group as defined above and n is an integer ranging from 1 to 5.

[0040] Typically, an excess of phenol (W_p) with respect to sulfonic acid (S_A) is used. Preferably, phenol (W_p) is used in a molar ratio of 1.3 with respect to sulfonic acid (S_A). More preferably, the molar ratio between phenol (W_p) and sulfonic acid (S_A) ranges from 1.1 to 1.5.

[0041] Sulfonic acid (A_S) and phenol (W_p) are placed into contact in a reactor at room temperature, and then heated to a temperature typically ranging from 100°C to 200°C and for a time ranging from 1 to 5 hours. A person skilled in the art will be able to determine the reaction temperature and time according to known methods on a case-by-case basis according to sulfonic acid (A_S) and phenol (W_p). In any case, the completion of the reaction can be followed withdrawing a sample and by submitting the samples to ^{19}F -NMR. The reaction is complete when shifts from -112 ppm ($-\text{CFSO}_3\text{H}$ signal) to -114.5 ppm ($-\text{CF}_2\text{-SO}_3\text{-Ar}$ signal) and -122 ($-\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ signal) to -121 ppm ($-\text{CF}_2\text{CF}_2\text{SO}_3\text{-Ar}$ signal) are observed.

[0042] The resulting sulfonic ester (E_S) is recovered from the reaction mixture according to methods known in the art, typically distillation, which can be chosen by the person skilled in the art on a case-by-case basis.

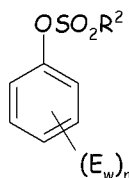
[0043] If sulfonic acid (A_S) is an acid (S_{A-1}) as defined above, the resulting sulfonic ester (E_S) is an ester (E_{S-1}) complying with formula:

(E_S-1)

wherein R¹, E_w and n are as defined above.

[0044] Sulfonic ester (E_S-1) in which R¹ is -CF₃, E_w is -NO₂ and n is 1 is a preferred embodiment of the present invention. Indeed, as explained in detail below, it can be most advantageously used as sulfonating agent of alcohols having a pK_a lower than 15.

[0045] If sulfonic acid (A_S) is an acid (S_A-2) as defined above, the resulting ester (E_S) is an ester (E_S-2) complying with formula:

(E_S-2)

wherein R², E_w and n are as defined above.

Method (M-1) – step c)

[0046] In step c), the alkali- or alkali-earth metal halide [herein after “metal halide (MX_{n'})”] is a halide of an alkali- or alkali-earth metal [metal (M)], i. e. a metal belonging to Group I or Group II of the periodic table.

Advantageously, metal (M) is selected from Li, Na, K, Mg and Ca; more preferably, the metal is Li or Na.

[0047] Advantageously, in halide (MX_{n'}), X is a halogen selected from fluorine or chlorine and n' is 1 or 2; preferably, X is fluorine.

[0048] According to a preferred aspect of the invention, metal halide (MX_{n'}) is KF.

[0049] An excess of metal halide (MX_{n'}) with respect to sulfonic ester (E_S) is typically used in step c).

[0050] Advantageously, metal halide (MX_{n'}) is used in a molar ratio of at least 1.2:1 with respect to ester (E_S); preferably, the molar ratio between metal halide (MX_{n'}) and sulfonic ester (E_S) ranges from 1.5 to 2.5.

[0051] Sulfonic ester (E_S) and metal halide (MX_{n'}) are contacted into a reactor in

the presence of a polar organic solvent, to provide a mixture that is heated to the solvent's reflux temperature for a time typically ranging from 50°C to 100°C and for a time typically ranging from 1 to 5 hours.

- [0052] The polar organic solvent is advantageously selected from dimethylsulfoxide, sulfolane, dimethylacetamide and acetonitrile; according to a preferred embodiment, the solvent is acetonitrile.
- [0053] The reaction time can be determined by the person skilled in the art on a case-by-case basis according to sulfonic ester (E_S) and metal halide (MX_n). In any case, the completion of the reaction can be followed by withdrawing a sample and submitting the sample to ^{19}F -NMR. The reaction is complete when appearance of a signal at +48 ppm ($-\text{SO}_2\text{E}$) is observed.
- [0054] The resulting sulfonyl halide (A_{SH}) is recovered from the reaction mixture according to methods known in the art, typically distillation, which can be chosen by the person skilled in the art on a case-by-case basis.
- [0055] If sulfonic ester (E_S) is an ester (E_{S-1}) as defined above, the sulfonyl halide (A_{SH}) is a sulfonyl halide (A_{SH-1}) of formula:
 $(A_{SH-1}) \text{ R}^1\text{-SO}_2\text{X}$
 wherein R^1 and X are as defined above.
- [0056] If sulfonyl ester (E_S) is an ester (E_{S-2}) as defined above, the sulfonyl halide (A_{SH}) is a sulfonyl halide (A_{SH-2}) of formula:
 $(A_{SH-2}) \text{ R}^2\text{-SO}_2\text{X}$
 wherein R^1 and X are as defined above.

Method (M-2)

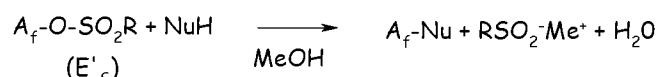
- [0057] As mentioned above, method (M-1) can be advantageously used to obtain sulfonic esters (E_S) or sulfonyl halides (A_{SH}) from sulfonic acids salts (S) separated from reaction mixtures comprising said sulfonic salts (S) as by-products.
- [0058] Accordingly, in a preferred embodiment, the present invention further relates to a method (M-2) which comprises a step a₀) comprising isolating a sulfonic acid salt (S) from a reaction mixture and then submitting salt (S) to steps a) – c) as defined above.
- [0059] Accordingly, method (M-2) comprises the following steps:

- a₀) isolating a sulfonic acid salt (S) from a reaction mixture;
- a) reacting a sulfonic acid [salt (S)] with a strong mineral acid [acid (A_M)] to provide the corresponding fluorinated sulfonic acid [acid (A_S)];
- b) reacting the fluorinated sulfonic acid (A_S) from step a) with a phenol substituted with at least one electron-withdrawing group to provide the corresponding ester of sulfonic acid (A_S) [sulfonic ester (E_S)]; and, optionally
- c) reacting ester (E_S) with an anhydrous alkali- or alkali-earth metal halide to provide the corresponding fluorinated sulfonyl halide [sulfonyl halide (A_{SH})].

[0060] Advantageously, the mixture is one obtained from the reaction of a fluorinated sulfonic ester of a fluorinated alcohol [ester (E'_S)] of formula :

$$A_f-O-SO_2R$$

with a reagent NuH, according to the following equation (1):



wherein:

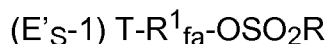
- R is as defined above;
- A_f is a (per)fluoroalkyl or (per)fluoro(poly)oxyalkyl chain, optionally comprising one or more -OSO₂R groups, with the condition that A_f is selected in such a way that its electron-withdrawing power is lower than that of the -OSO₂R groups, which means that a corresponding alcohol A_f-OH, wherein A_f is as defined above, must have a pK_a at most of 13, and preferably ranging from 7.5 to 13; and
- NuH is a nucleophile reagent.

[0061] Usually, in order for A_f to have an electron-withdrawing power lower than that of the -OSO₂R group, as defined above, it is selected in such a way as the carbon atom directly bound to the -OSO₂R group does not bear fluorine atoms. In other words, it is a fluoroalkyl or a fluoro(poly)oxyalkyl chain comprising a -CH₂- group, a secondary carbon atom (-CH-) or a tertiary carbon atom directly bound to the -OSO₂R group.

[0062] Non limiting examples of NuH reagents include aliphatic and aromatic alcohols, amines and thiols, but also carbon-anions.

[0063] Typically, R is a group R^1 or R^2 as defined above, preferably a chain R^1 . Preferred examples of groups R^1 are trifluoromethyl, pentafluoroethyl, heptafluoroethyl and nonafluorobutyl, trifluoromethyl and nonafluorobutyl being more preferred.

[0064] In a first preferred aspect, sulfonic ester (E'_s) is a sulfonic ester of a (per)fluoroalkyl alcohol, wherein A_f is a (per)fluoroalkyl chain optionally comprising one or more $-OSO_2R$ groups. Advantageously, according to this aspect, ester (E'_s) is an ester (E'_s-1) complying with formula:



wherein:

- T is (per)fluoromethyl or $-OSO_2R$;
- R is as defined above and
- R^1_{fa} is a straight or branched fluoroalkylene chain comprising from 1 to 10 carbon atoms, preferably from 1 to 4 carbon atoms, with the proviso that it contains a $-CH_2-$ group or a tertiary C-atom directly bound to the $-OSO_2R$ group(s).

[0065] In a second preferred aspect, sulfonic ester (E'_s) is a sulfonic ester of a PFPE alcohol, wherein A_f is a straight or branched fluoro(poly)oxyalkylene chain, optionally comprising one or more $-OSO_2R$ groups.

Advantageously, according to this aspect, ester (E'_s) is an ester (E'_s-2) complying with formula:



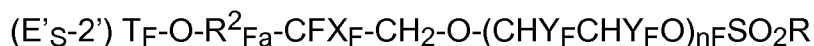
wherein:

- T' is a (per)haloalkyl or a $-SO_2R$ group;
- R is as defined above and
- R^2_{fa} is a fluoro(poly)oxyalkylene chain comprising recurring units (R°) selected from:
 - (i) $-CFX_fO-$, wherein X is F or CF_3 ;
 - (ii) $-CFX_fCFX_fO-$, wherein X_f , equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X_f is $-F$;
 - (iii) $-CF_2CF_2CW_fO-$, wherein each of W_f , equal or different from each other, is F, Cl, H,
 - (iv) $-CF_2CF_2CF_2CF_2O-$;

(v) $-(CF_2)_j-CFZ_f-O-$ wherein j is an integer from 0 to 3 and Z_f is a group of general formula $-OR^*_{af}T$, wherein R^*_{af} is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : $-CFX_fO-$, $-CF_2CFX_fO-$, $-CF_2CF_2CF_2O-$, $-CF_2CF_2CF_2CF_2O-$, with each of each of X_f being independently F or CF_3 and T' is a (per)haloalkyl group with the proviso that chain R^2_{fa} contains a $-CH_2-$ group or a tertiary C-atom directly bound to the $-OSO_2R$ group(s).

[0066] In one preferred embodiment, esters (E'_S-2) are monofunctional, i.e. they have an average functionality (F) lower than 1.2, while in another preferred embodiment they are bifunctional, i.e. they have an average functionality (F) higher than 1.90.

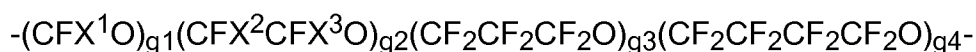
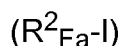
[0067] According to a preferred embodiment, ester (E'_S-2) complies with formula (E'_S-2'):



wherein:

- T_F is $-CFX_F-CH_2-O-(CHY_FCHY_FO)_{nF}SO_2R$ or a (per)haloalkyl group, typically a C_1 - C_3 haloalkyl group, preferably selected from $-CF_3$, $-CF_2Cl$, $-CF_2CF_2Cl$, $-C_3F_6Cl$, $-CF_2Br$, $-CF_2CF_3$ and $-CF_2H$, $-CF_2CF_2H$;
- R^2_{Fa} is a PFPE chain comprising recurring units (i) – (v) as defined above;
- X_F is F or CF_3 , preferably F;
- Y_F is, independently of each other, hydrogen or lower alkyl, typically C_1 - C_4 alkyl, preferably methyl;
- n_F is 0 or a positive number preferably ranging from 1 to 10 and
- R is as defined above.

[0068] Preferably, chain R^2_{Fa} complies with formula (R^2_{Fa-I}):



wherein:

- X^1 is independently selected from $-F$ and $-CF_3$;
- X^2 , X^3 , equal or different from each other and at each occurrence, are independently $-F$, $-CF_3$, with the proviso that at least one of X is $-F$;

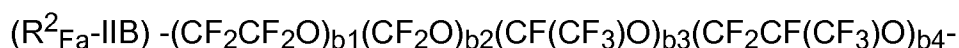
- g_1 , g_2 , g_3 , and g_4 , equal or different from each other, are independently integers ≥ 0 , such that $g_1+g_2+g_3+g_4$ is in the range from 2 to 300, preferably from 2 to 100; should at least two of g_1 , g_2 , g_3 and g_4 be different from zero, the different recurring units are generally statistically distributed along the chain.

[0069] More preferably, chain (R^2_{Fa}) is selected from chains of formulae (R^2_{Fa} -IIA) - (R^2_{Fa} -IIE):



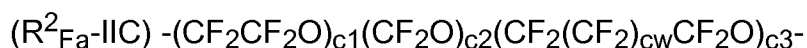
wherein:

- a_1 and a_2 are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; both a_1 and a_2 are preferably different from zero, with the ratio a_1/a_2 being preferably comprised between 0.1 and 10;



wherein:

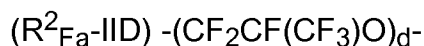
- b_1 , b_2 , b_3 , b_4 , are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; preferably b_1 is 0, b_2 , b_3 , b_4 are > 0 , with the ratio $b_4/(b_2+b_3)$ being ≥ 1 ;



wherein:

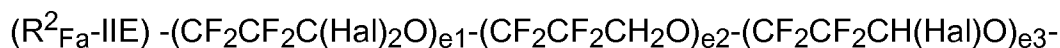
- $cw = 1$ or 2 ;

c_1 , c_2 , and c_3 are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; preferably c_1 , c_2 and c_3 are all > 0 , with the ratio $c_3/(c_1+c_2)$ being generally lower than 0.2;



wherein:

- d is an integer > 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000;



wherein:

- Hal, equal or different at each occurrence, is a halogen selected from

fluorine and chlorine atoms, preferably a fluorine atom;

- e1, e2, and e3, equal to or different from each other, are independently integers ≥ 0 such that the (e1+e2+e3) sum is comprised between 2 and 300.

[0070] Still more preferably, chain (R^2_{Fa}) complies with formula (R^2_{Fa} -III) here below:



wherein:

- a1, and a2 are integers > 0 such that the number average molecular weight is between 400 and 4,000, with the ratio a2/a1 being generally comprised between 0.2 and 5.

[0071] Most conveniently, method (M-2) is applied to PFPE esters (E'_S -2), more preferably to bifunctional esters of formula (E'_S -2') as defined above in which:

- R^2_{Fa} complies with formula (R^2_{Fa} -III);

- X_F is fluorine;

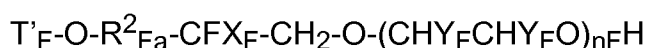
- Y_F is H;

- n_F is 0 or a positive number ranging from 1 to 10 and

- R is as defined above.

[0072] Sulfonic esters (E'_S) can be obtained according to methods known in the art by reaction of a fluorinated alcohol [alcohol (A_{OH})] with a sulfonyl halide (A_{SH}).

[0073] In particular, esters (E'_S -2) can be obtained by reaction of a PFPE alcohol [alcohol (A_{OH} -1)] comprising at least one $-\text{CH}_2\text{OH}$ group according to methods known in the art, for example following the teaching of **TONELLI, et al.** Linear perfluoropolyether difunctional oligomers: chemistry, properties and applications. *Journal of Fluorine Chemistry*. 1999, vol.95, p.51 - 70. **Tonelli, et al.** Linear perfluoropolyether difunctional oligomers: chemistry, properties and applications. *Journal of Fluorine Chemistry*. 1999, vol.95, p.51-70. , in particular as reported on page 64, par. 3.2.15. Esters (E'_S -2') can be obtained according to such method using a PFPE alcohol [alcohol (A_{OH} -2)] of formula:



wherein:

T' is the same as T_F or a -CH₂-O-(CHY_FCHY_FO)_{nF}H group;

and R²_{Fa}, X_F, Y_F and n_F are as defined above,

said alcohol (A_{OH-2}) having a functionality higher than 1.90.

- [0074] Perfluoropolyether alcohols are known in the art and can be manufactured according to known methods. In particular, PFPE alcohols (A_{OH-2}) in which R²_{Fa} complies with formula (R²_{Fa} -III) and n_F = 0 are commercially available from Solvay Specialty Polymers Italy S.p.A. with trade name Fomblin[®]. Corresponding PFPE alcohols wherein n_F is equal to or higher than 1 can be obtained by reaction of a Fomblin[®] PFPE with an epoxide in the presence of a base, according to known methods.

Method (M-3)

- [0075] As stated above, either ester (E_S) or sulfonyl halide (A_{SH}) obtained according to method (M-1) or to method (M-2) can be used as sulfonating agents for alcohols having a pK_a lower than 15 to provide the corresponding sulfonic esters. Such alcohols comprise both aromatic alcohols and fluorinated alcohols A_F-OH as defined above.
- [0076] Accordingly, in a further preferred aspect, the present invention relates to a method [method (M-3)] for obtaining a sulfonic ester of a PFPE alcohol which comprises the following steps:
- a) reacting a salt of a fluorinated sulfonic acid [salt (S)] with a strong mineral acid [acid (A_M)] to provide the corresponding fluorinated sulfonic acid [acid (A_S)];
 - b) reacting the fluorinated sulfonic acid (A_S) from step a) with a phenol substituted with at least one electron-withdrawing group to provide the corresponding ester of sulfonic acid (A_S) [sulfonic ester (E_S)];
 - c) optionally reacting ester (E_S) with an anhydrous alkali- or alkali-earth metal halide to provide the corresponding fluorinated sulfonyl halide [sulfonyl halide (A_{SH})];
 - d) reacting ester (E_S) or sulfonyl halide (A_{SH}) with an alcohol having a pK_a lower than 15 to provide the corresponding sulfonic ester [sulfonic ester (E*_S)].
- [0077] If only steps a), b) and d) are carried out in method (M-3), and if the

alcohol having a pK_a lower than 15 is an alcohol of formula $A_f\text{-OH}$ wherein A_f is as defined above, sulfonic ester (E^*_S) complies with formula (E^*_s):
 $A_f\text{-O-SO}_2R^*$

wherein A_f is as defined above and R^* is a phenol group substituted with at least one electron-withdrawing group (E_w) as defined above.

[0078] If the alcohol having a pK_a lower than 15 is an alcohol of formula $A_f\text{-OH}$ wherein A_f is as defined above and all steps a) – d) are carried out in method (M-3), sulfonic ester (E^*_S) complies with formula (E'_S) as defined above.

[0079] According to a preferred aspect, sulfonic salt (S) is obtained from the reaction of a sulfonic ester (E'_S) with a nucleophile reagent, according to equation (1) depicted above.

[0080] Thus, the present invention further comprises a method [method (M-3')] which comprises the following steps:

a') reacting a sulfonic ester (E'_S) as defined above with a nucleophile compound, to provide a mixture comprising a sulfonic salt (S) as defined above;

a'') isolating sulfonic salt (S) from the mixture;

a) reacting sulfonate salt (S) with a strong mineral acid [acid (A_M)] to provide the corresponding fluorinated sulfonic acid [acid (A_S)];

b) reacting the fluorinated sulfonic acid (A_S) from step a) with a phenol [phenol (W_p)] substituted with at least one electron-withdrawing group to provide the corresponding ester of sulfonic acid (A_S) [sulfonic ester (E_S)];

c) optionally reacting ester (E_S) with an anhydrous alkali- or alkali-earth metal halide to provide the corresponding fluorinated sulfonyl halide [sulfonyl halide (A_{SH})];

d) reacting ester (E_S) or sulfonyl halide (A_{SH}) with a fluorinated alcohol to provide the corresponding sulfonic ester (E^*_S).

[0081] According to a preferred embodiment of the invention, sulfonic ester (E_S) is used as sulfonating agent; thus, in order to obtain this ester, optional step c) is not carried out in process (M-1) and in preferred processes (M-2) and (M-3).

[0082] The omission of step c) is particularly useful in cases where sulfonate salt

(S) is a trifluoromethanesulfonate salt. Indeed, carrying out step c) would lead to the obtainment of trifluoromethanesulfonyl chloride, which is a gas difficult to handle, so much so that trifluoromethanesulfonyl anhydride ($\text{CF}_3\text{SO}_2)_2\text{O}$ is typically used as sulfonating agent, which can be most conveniently stored and handled; however, $(\text{CF}_3\text{SO}_2)_2\text{O}$ is considerably expensive.

[0083] The omission of step c) is particularly convenient on an industrial scale, because ester (E_S) can be reacted with an alcohol having a pK_a lower than 15, preferably with a fluorinated alcohol, to provide an ester (E^*s), which can be reacted with a nucleophile compound to provide a mixture comprising a sulfonate salt (S); salt (S) can then be isolated and submitted to steps a), b) and d) according to preferred method (M-3').

[0084] Therefore, the present invention further relates to a process [process (M-3'')] comprising the following steps:

a') reacting an ester (E'_S) as defined above with a nucleophile compound as defined above, to provide a mixture comprising a sulfonate salt (S);
 a'') isolating sulfonate salt (S) from the mixture;
 a) reacting sulfonate salt (S) with a strong mineral acid [acid (A_M)] to provide the corresponding fluorinated sulfonic acid [acid (A_S)];
 b) reacting the fluorinated sulfonic acid (A_S) from step a) with a phenol substituted with at least one electron-withdrawing group to provide the corresponding ester of sulfonic acid (A_S) [sulfonic ester (E_S)];
 d) reacting ester (E_S) with an alcohol having a pK_a lower than 15 to provide the corresponding sulfonic ester (E^*s); and optionally
 e) reacting sulfonic ester (E^*s) with a nucleophile compound, to provide a mixture comprising a sulfonic salt (S) and recycling sulfonic ester (E^*s) to step a') and repeating steps a'') – d) or a'') - e).

[0085] According to a particularly preferred embodiment, in process (M-3''), ester (E'_S) is a PFPE ester complying with formula (E'_S -2) as defined above. Preferably, it is a bifunctional ester of formula (E'_S -2') as defined above in which:

- R^2_{Fa} complies with formula (R^2_{Fa} -III);
- X_F is fluorine;

- Y_F is H;
- n_F is 0 or a positive number ranging from 1 to 0 and
- R is as defined above.

[0086] Advantageously, method (M-3'') is applied to esters (E'_S) in which R is trifluoromethyl.

[0087] The invention will be illustrated in greater detail in the following Experimental section by means of non-limiting examples.

[0088] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Experimental section

Material and methods

[0089] All reagents were used as received by the manufacturer without further purification. The solvent (acetonitrile) was previously distilled and maintained over molecular sieves.

Example 1

[0090] **Step a) Conversion of perfluorobutane sulfonate sodium salt into perfluorobutane sulfonic acid**

[0091] Anhydrous sulfuric acid (37 g, 360 mmols) was placed in a glass round-bottomed flask equipped with a magnetic stir bar, a reflux condenser, a thermometer and a solid dispenser. Perfluorobutane sulfonate sodium salt (C₄F₉SO₃Na, 35 g, 109 mmols) was placed in the dispenser and added to the acid in 10 minutes. No exothermic reaction was observed. The mixture was stirred at 120°C for 30 minutes at 1,000 rpms. The progress of the reaction was followed by ¹⁹F-NMR. Once complete conversion of acid was observed (the -CF₂-SO₃H peak shifted from -114.5 ppm to -112 ppm and the -CF₂CF₂SO₃H peak shifted from -121 ppm to -122 ppm; total shift = 3.5 ppms), the internal temperature was raised to 140°C and vacuum (0.8 mbar residual pressure) was applied to the reaction mixture to distil perfluorobutane sulfonic acid as a clear liquid.

[0092] Yield: 28.1 g (94 mmols); 94 mol%.

[0093] **Step b) Conversion of perfluorobutane sulfonic acid into perfluorobutane *para*-nitro phenyl sulfonate**

[0094] Perfluorobutane sulfonic acid (25 g, 83 mmols) from step a), was placed in a glass reactor identical to the one used for step a) and *para*-nitrophenol was added (30 g, 216 mmols) at room temperature in about 20 minutes. The reaction temperature was raised to 150°C with 900 rpm stirring for 3.5 hrs. During the course of the reaction the reaction mixture turned deep red. The progress of the reaction was followed by ^{19}F -NMR. Once the conversion of the acid to the corresponding *para*-nitro phenyl ester was completed (the $-\text{CF}_2\text{SO}_3\text{-Ar}$ peak shifted to -114.3 ppm and the $-\text{CF}_2\text{CF}_2\text{SO}_3\text{-Ar}$ peak shifted to -121 ppm; a total shift = 3 ppm), the reaction mixture was distilled at 160°C and 0.9 residual mbar pressure. The distillate was a pale yellow liquid that became an off-white, crystalline solid at room temperature.

[0095] Yield: 33 g (92 mol%); 76 mmols.

[0096] **Step c) Conversion of perfluorobutane *para*-nitro phenyl sulfonate into perfluorobutane sulfonyl fluoride**

[0097] Perfluorobutane *para*-nitrophenyl sulfonate from step b) (15 g, 34 mmols) was dissolved in anhydrous CH_3CN (60 ml) in a glass reactor equipped with a reflux condenser, a heating oil-bath, an internal thermometer, a dropping funnel and a magnetic stirring bar. Anhydrous KF (4 g, 69 mmol) was added. and mixture was heated to the solvent's reflux temperature (i.e. about 80°C). The water condenser maintained all products in the reactor, until complete conversion. The progress of the reaction was followed by ^{19}F -NMR. During the course of the conversion the colourless solution turned yellow. Once the ^{19}F -NMR analysis showed complete conversion (the $-\text{CF}_2\text{SO}_2\text{F}$ peak shifted to -108 ppm and the $-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ peak shifted to -122; a total shift = 7 ppm). The new fundamental peak of $-\text{SO}_2\text{F}$ appeared at + 48 ppm and integrated 50% of the area of each of the peaks at -108, -122 and -126 ppm), the desired perfluorobutane sulfonyl fluoride was isolated by distillation (b.p. 60°C). Some product was also successfully isolated from the acetonitrile solvent by a quick washing in ice-cold water; the product separated as a colourless liquid in the

bottom layer.

[0098] Yield 10.3 g (32 mmols), 93 mol%.

[0099] Overall yield of perfluorobutane sulfonyl fluoride: 80.7%.

[0100] **Example 1A**

[0101] Example 1 was repeated using, as esterifying agent, 4-cyanophenol instead of 4-nitrophenol.

[0102] The overall yield of the target perfluorobutane sulfonyl fluoride was 82%.

Example 2

[0103] **Step a) Conversion of perfluoroethane sulfonate sodium salt into perfluorobutane sulfonic acid**

[0104] Anhydrous sulfuric acid (50 g, 487 mmols) was placed in a glass round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, a thermometer and a solid dispenser. Perfluoroethane sulfonate sodium salt ($\text{C}_2\text{F}_5\text{SO}_3\text{Na}$, 20 g, 90 mmols) was placed into the solid dispenser and added to the acid in 10 minutes. No exothermic reaction was observed. The mixture was stirred at 120°C for 30 minutes at 1,000 rpms. The progress of the reaction was followed by ^{19}F -NMR. Once complete conversion of the acid was observed (same chemical shifts observed as in Example 1, step a), the internal temperature was raised to 120°C and vacuum (1 mbar residual pressure) was applied to the reaction mixture to distil the perfluoroethane sulfonic acid as a clear liquid.

[0105] Yield: 17 g (85 mmols); 94 mol%.

[0106] **Step b) Conversion of perfluorobutane sulfonic acid into perfluoroethane *para*-nitrophenyl sulfonate**

[0107] Perfluoroethane sulfonic acid (25 g, 125 mmols) from step a) was placed in a glass reactor identical to that use in step a) and *para*-nitrophenol (30 g, 216 mmols) was added at room temperature in about 20 minutes. The reaction temperature was raised to 150°C with 900 rpm stirring for 3.5 hrs. During the course of the reaction, the reaction mixture turned deep red. The progress of the reaction was followed by ^{19}F -NMR. Once the conversion of the acid to the corresponding phenylester was completed (same chemical shifts as observed in Example 1, step b), the reaction mixture was distilled at 160°C and 0.9 residual mbar pressure. The

distillate was a pale yellow liquid which solidified at room temperature becoming an off-white, crystalline solid.

[0108] Yield: 37.7g (117 mmols); 94 mol%.

[0109] **Step c) Conversion of perfluoroethane *para*-nitrophenyl sulfonate into perfluoroethanesulfonyl fluoride**

[0110] Perfluoroethane *para*-nitrophenyl sulfonate (20 g, 62 mmols) from step b) was dissolved in anhydrous CH₃CN (70 ml) to which anhydrous KF (5g, 86 mmol) was added. The reaction temperature was maintained at the reflux temperature of the solvent (ca. 80°C) and the just formed perfluoroethane sulfonyl fluoride was distilled off and collected in an ice-cooled flask. The progress of the reaction was followed by ¹⁹F-NMR analysis. During the course of the reaction the colourless solution became yellow. Once the ¹⁹F-NMR analysis showed complete conversion (same chemical shifts as observed in Example 1, step a), the desired perfluoroethanesulfonyl fluoride was completely removed from the reaction mass (b.p. ca. 20°C). Some product was also successfully isolated by a quick washing in ice-cold water from the residual acetonitrile solvent. The desired product separated as a colourless liquid in the bottom layer.

[0111] Yield :12.8 g (59 mmols); 95 mol%.

[0112] Overall yield 83.9%

Example 3

[0113] **Synthesis of Fomblin® Z DOL PFPE nonaflate starting from perfluorobutane *para*-nitro phenyl sulfonate**

[0114] A glass reactor was charged with perfluorobutane *para*-nitro phenyl sulfonate (17.7 g, 40.8 meq) prepared accordingly to Example 1. The internal temperature of the reaction mass was maintained at room temperature. Fomblin® Z DOL PFPE (20 g, 38 meq) of formula:
 $\text{HOCH}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{O})_{a1}(\text{CF}_2\text{O})_{a2}\text{CF}_2\text{CH}_2\text{OH}$
(where a1 and a2 as defined above and are selected in such a way as the MW is 1,000 and EW is 500; a1/a2 = 2)
was added drop-wise under vigorous stirring. Thereafter, the reaction mass was warmed up to room temperature, under mechanical stirring. The reaction was monitored by ¹⁹F-NMR analysis. After 1 hour at room

temperature a sample was taken for NMR analysis and the observed conversion of the hydroxy groups into perfluorobutanesulfonate groups was 70%. The internal temperature was increased to 70°C until completion of the reaction. After complete conversion, the reaction mass was cooled to room temperature and the product was washed twice with ethanol (20 g each time). The organic phase was separated and ethanol was stripped at 70°C under vacuum. The resulting product (Fomblin[®] Z DOL PFPE nonaflate) was isolated with a purity > 96% and a yield > 90%. The typical diagnostic ¹⁹F-NMR signals of this product resonate at -107.5 ppm, while the diagnostic peak of any perfluorosulfonate (hydrolysed nonaflate) resonates at -111.5 ppm. The resulting Fomblin[®] Z DOL PFPE nonaflate had a MW of 1,630 and an EW of 820.

Claims

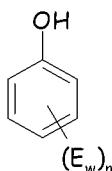
1. A method for the obtainment of an ester or a halide of a fluorinated sulfonic acid from a salt of a sulfonic acid, said process comprising the following steps:
 - a) reacting a salt of a fluorinated sulfonic acid [salt (S)] with a mineral acid [acid (A_M)] having a pK_a lower than 0 to provide the corresponding fluorinated sulfonic acid [acid (A_S)];
 - b) reacting the fluorinated sulfonic acid (A_S) from step a) with a phenol [phenol (W_p)] substituted with at least one electron-withdrawing group selected from one or more of nitro, cyano, perfluoro alkyl and fluorine to provide the corresponding ester of sulfonic acid (A_S) [sulfonic ester (E_S)]; and, optionally
 - c) reacting ester (E_S) with an anhydrous alkali- or alkali-earth metal halide to provide the corresponding fluorinated sulfonyl halide [sulfonyl halide (A_{SH})].
2. The method according to claim 1, wherein salt (S) is an alkali- or alkali-metal salt.
3. The method according to claim 2, wherein salt (S) complies with formula:

$$R-SO_3^-Me^+$$
 wherein:
 - R is a (per)fluoroalkyl or a (per)fluoro(poly)oxyalkyl chain comprising a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group and
 - Me^+ is an alkali metal cation.
4. The method according to claim 3, wherein salt (S) complies with formula:

$$(S-1) R^1-SO_3^-Me^+,$$
 wherein:
 - R^1 is a C_1-C_{10} (per)fluoroalkyl chain, with the proviso that chain R^1 contains a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group and
 - Me^+ is an alkali metal cation.
5. The method according to claim 3, wherein salt (S) complies with formula:

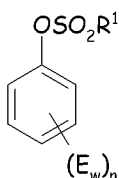
$$(S-2) R^2-SO_3^-Me^+$$
 wherein:
 - R^2 is a straight or branched C_1-C_{10} (per)fluoro(poly)oxyalkyl chain, with the proviso that chain R^2 contains a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group; and
 - Me^+ is an alkali metal cation.

6. The method according to any one of claims 1 to 5 wherein acid (A_M) is fluorosulfonic or sulphuric acid.
7. The method according to any one of claims 1 to 6 wherein phenol (W_p) complies with formula:



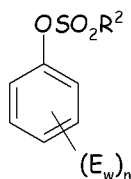
wherein E_w is an electron-withdrawing group as defined in claim 1 and n is an integer ranging from 1 to 5.

8. The method according to claim 7 wherein phenol (W_p) is 4-nitrophenol or 4-cyanophenol.
9. The method according to any one of claims 1 to 8 wherein ester (E_s) complies with formula:
(E_S-1)



wherein:

- R^1 is a C_1 - C_{10} (per)fluoroalkyl chain, with the proviso that chain R^1 contains a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group;
 - E_w is an electron-withdrawing group selected from one or more of nitro, cyano, perfluoro alkyl and fluorine and n is an integer ranging from 1 to 5.
10. The method according to any one of claims 1 to 8 wherein ester (E_s) complies with formula:
(E_S-2)



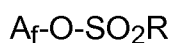
wherein:

- R^2 is a straight or branched C_1 - C_{10} (per)fluoro(poly)oxyalkyl chain, with the proviso that chain R^2 contains a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group;

- E_w is an electron-withdrawing group selected from one or more of nitro, cyano, perfluoro alkyl and fluorine and

- n is an integer ranging from 1 to 5.

11. A method for the obtainment of an ester or a halide of a fluorinated sulfonic acid from a salt of a sulfonic acid which comprises a step a_0) wherein a sulfonic acid salt (S) is isolated from a reaction mixture; and submitting salt (S) to steps (a) – (c) according to any one of claims 1 to 10.
12. The method according to claim 11 wherein the reaction mixture is obtained by reaction of a fluorinated sulfonic ester (E'_S) of formula:



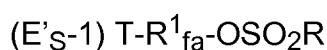
wherein:

- R is a (per)fluoroalkyl or a (per)fluoro(poly)oxyalkyl chain comprising a $-CF_2-$ group directly bound to the sulphur atom of the $-SO_3^-$ group;

- A_f is a (per)fluoroalkyl or (per)fluoro(poly)oxyalkyl chain selected in such a way as the carbon atom directly bound to the $-OSO_2R$ group does not bear fluorine atoms

with a nucleophile reagent.

13. The method according to claim 12 wherein ester (E'_S) complies with formula:



wherein:

- T is (per)fluoromethyl or $-\text{OSO}_2\text{R}$;
- R is a (per)fluoroalkyl or a (per)fluoro(poly)oxyalkyl chain comprising a $-\text{CF}_2-$ group directly bound to the sulphur atom of the $-\text{SO}_3^-$ group and
- R_{fa}^1 is a straight or branched fluoroalkylene chain comprising from 1 to 10 carbon atoms, with the proviso that it contains a $-\text{CH}_2-$ group or a tertiary carbon atom directly bound to the $-\text{OSO}_2\text{R}$ group(s).

14. The method according to claim 12 wherein ester (E'_{S}) complies with formula:

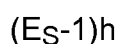


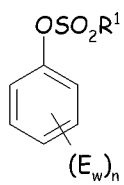
wherein:

- T' is a (per)haloalkyl or a $-\text{SO}_2\text{R}$ group;
- R is a (per)fluoroalkyl or a (per)fluoro(poly)oxyalkyl chain comprising a $-\text{CF}_2-$ group directly bound to the sulphur atom of the $-\text{SO}_3^-$ group and
- R_{fa}^2 is a fluoro(poly)oxyalkylene chain comprising recurring units (R°) selected from:

- (i) $-\text{CFX}_f\text{O}-$, wherein X is F or CF_3 ;
 - (ii) $-\text{CFX}_f\text{CFX}_f\text{O}-$, wherein X_f , equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X_f is $-\text{F}$;
 - (iii) $-\text{CF}_2\text{CF}_2\text{CW}_f\text{O}-$, wherein each of W_f , equal or different from each other, is F, Cl, H,
 - (iv) $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$;
 - (v) $-(\text{CF}_2)_j-\text{CFZ}_f\text{O}-$ wherein j is an integer from 0 to 3 and Z_f is a group of general formula $-\text{OR}_{\text{af}}^*\text{T}$, wherein R_{af}^* is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : $-\text{CFX}_f\text{O}-$, $-\text{CF}_2\text{CFX}_f\text{O}-$, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$, with each of each of X_f being independently F or CF_3 and T' is a (per)haloalkyl group
- with the proviso that chain R_{fa}^2 contains a $-\text{CH}_2-$ group directly bound to the $-\text{OSO}_2\text{R}$ group(s).

15. A sulfonic ester complying with formula:





in which R^1 is $-\text{CF}_3$, E_w is $-\text{NO}_2$ and n is 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/067230

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C303/02 C07C303/28 C07C309/65
ADD.

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	L. CONTE ET AL: "A new method for recovering waste alkaline perfluoro-n-butanesulfonate", JOURNAL OF FLUORINE CHEMISTRY, vol. 53, no. 2, 1 July 1991 (1991-07-01), pages 277-283, XP055220321, NL ISSN: 0022-1139, DOI: 10.1016/S0022-1139(00)82346-5 cited in the application page 277, summary page 278, lines 14-20 page 279, paragraph 2 - page 280, last paragraph ----- -/--	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

4 October 2016

Date of mailing of the international search report

10/10/2016

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/067230

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DARRYL D. DIXON ET AL: "Heteroadamantyl Cannabinoids", JOURNAL OF MEDICINAL CHEMISTRY, vol. 53, no. 15, 12 August 2010 (2010-08-12), pages 5656-5666, XP055220395, US ISSN: 0022-2623, DOI: 10.1021/jm100390h page 5657, column 1, last four lines -----	1-15
A	US 3 681 076 A (SKOOG IVAN H) 1 August 1972 (1972-08-01) column 5, lines 28-39 -----	1-15
A	US 3 803 199 A (VOSS P ET AL) 9 April 1974 (1974-04-09) column 1, lines 49-67 examples 10,12,13 -----	1-15
A	MARIA J. V. DE OLIVEIRA BAPTISTA ET AL: "The relative nucleophilicities of fluoride and aryloxy ions towards acyl and nitroaryl groups", JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 1, no. 3, 1 January 1978 (1978-01-01), page 295, XP055220542, GB ISSN: 0300-922X, DOI: 10.1039/p19780000295 page 296; compounds 3,5 runs 9-11; page 296 -----	1-15
A	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SAKAI, SHIGENORI ET AL: "Method for purification of trifluoromethanesulfonyl fluoride", XP002752586, retrieved from STN Database accession no. 2010:332748 abstract -& JP 2010 059071 A (CENTRAL GLASS CO LTD) 18 March 2010 (2010-03-18) the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/067230

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