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(71) Applicant: MINNESOTA MINING AND MANUFACTUR-ING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: HOWELLS, Richard, D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LAMANNA, William, M.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). FANTA, Alan, D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). WADDELL, Jennifer, E.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: SCHULTE, Daniel, C. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

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(54) Title: PREPARATION OF BIS(FLUOROALKYLENESULFONYL)IMIDES AND (FLUOROALKYLSULFONYL) (FLUOROSUL-FONYL)IMIDES

(57) Abstract

A method for preparing fluoroalkylsulfonyl imides by reacting a fluoroalkylsulfonamide with a fluoroalkylsulfonyl halide or a fluorosulfonyl halide in the presence of a non-nucleophilic base. One reaction is: $Z-R_f-SO_2NH_2 + Z-R'_f-SO_2-X + 2B \Rightarrow (Z-R_f-SO_2)(Z-R'_f-SO_2)N^-\cdot BH^+ + BHX$, where each Z is a fluorine atom or a polymerizable organic functional group, R_f and R'_f are fluoroalkylene groups optionally containing catenary oyxgen or nitrogen, X is a halogen atom, and B is a non-nucleophilic base. Unsymmetrical imides and polymeric imides can be prepared.

Preparation of Bis(fluoroalkylenesulfonyl)Imides and (Fluoroalkylsulfonyl)(Fluorosulfonyl)Imides

Technical Field

This invention relates to a method for
5   preparing bis(fluoroalkylsulfonyl)imides,
(fluoroalkylsulfonyl)(fluorosulfonyl)imides and
derivatives thereof.

Background

10   Bis(Fluoroalkylsulfonyl)imides,
(fluoroalkylsulfonyl)(fluorosulfonyl)imides and
derivatives thereof are known to be useful in many
chemical processes and formulations. In solution, the
imides behave as strong acids due to the presence of
15   the electron-withdrawing fluoroalkylsulfonyl or
fluorosulfonyl groups and exhibit exceptional stability
under a variety of conditions. These compounds have
been found to be useful, for example, as fuel cell
electrolytes, as esterification catalysts and as
20   polymerization catalysts for cationically-sensitive
monomers such as epoxy resins.

The salts of bis(fluoroalkylsulfonyl)imides
and (fluoroalkylsulfonyl)(fluorosulfonyl)imides have
been found useful as electrolytes in advanced high
25   voltage batteries. In particular, lithium
bis(trifluoromethylsulfonyl)imide $(CF_3SO_2)_2N^-Li^+$, shows
excellent conductivity and stability, but can be
corrosive toward aluminum. Certain higher homologues
of this compound show comparable performance as battery
30   electrolytes, and have decreased the corrosion toward
aluminum.

There are several known methods for preparing
some classes of bis(fluoroalkylsulfonyl)imides.
Bis(perfluoroalkylsulfonyl)imides can be prepared by

the reaction of an alkali metal salt of an N-
trimethylsilyl perfluoroalkylsulfonamide with a
perfluoroalkylsulfonyl fluoride in a polar organic
solvent. This route requires several synthetic steps,
5   with the isolation of intermediate compounds, and the
overall yields are often low. A second method involves
the reaction of an alkali metal salts of a
perfluoroalkylsulfonamide with perfluoroalkylsulfonyl
fluoride in a polar organic solvent. Here too, the
10 yields are low. A third method involves reacting a
perfluorinated sulfonic anhydride with urea and a
sulfonic acid. The products of this reaction are then
dissolved in water and the addition of
tetrabutylammonium bromide precipitates the
15 tetrabutylammonium imide. This method is not
satisfactory for the large scale production of imides
because the overall yields are low and the sulfonic
anhydride precursors are not easily accessible. A
fourth method of making metal salts of sulfonimides
20 involves the reaction of a metal nitride with
perfluoroalkyl sulfonyl halide. However this method
cannot be used to make unsymmetrical imides and
requires handling metal nitrides which are sensitive to
air.

25   Thus there remains a need for an efficient
method of preparing bis(fluoroalkylsulfonyl)imides,
(fluoroalkylsulfonyl)(fluorosulfonyl)imides, and
derivatives thereof.

30 **Disclosure of the Invention**
            The present invention provides an efficient,
high yield method of preparing
bis(fluoroalkylsulfonyl)imides,
(fluoroalkylsulfonyl)(fluorosulfonyl)imides as well as
35 derivatives such as the organic or inorganic salts, and

N-halo, N-alkyl or N-silyl compounds; hereinafter
described as "imides" for the sake of brevity. The
method uses readily available starting materials and
allows the preparation of the imides in a single step,
5   without the isolation and purification of intermediate
compounds. The method of this invention also features
the preparation of unsymmetrical imides and polymers
having imide groups in the polymer chain.

By this method, a fluoroalkylsulfonamide is
10   contacted with a fluoroalkylsulfonyl halide or a
fluorosulfonyl halide, in the presence of a sufficient
amount of a non-nucleophilic base at a temperature and
for a time sufficient to yield the imide salt.
Preferably, the fluoroalkylsulfonamide is prepared *in*
15   *situ* by contacting a fluoroalkylsulfonyl halide with
anhydrous ammonia.

Detailed Description

In one aspect, the method of the invention
20   may be represented by the following Scheme 1:

Scheme 1

$Z-R_f-SO_2NH_2 + Z-R'_f-SO_2-X + 2B \Rightarrow (Z-R_f-SO_2)(Z-R'_f-SO_2)N^-$
$\cdot BH^+ + BHX,$
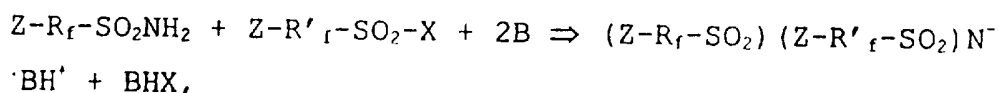
25   wherein R_f and R_f' are fluoroalkylene groups having
from 1 to 12 carbon atoms, optionally containing one or
more catenary oxygen or nitrogen atoms, each Z is a
fluorine atom or a polymerizable organic functional
group, X is a halogen atom and B is a non-nucleophilic
30   base. BH^+ represents an cation derived from the non-
nucleophilic base B, e.g. an ammonium cation, but other
cations may be used. In the case of symmetrical
imides, the sulfonamide is preferably generated *in situ*
by the reaction of a sulfonyl halide with anhydrous
35   ammonia. The sulfonamide then reacts with another

molecule of sulfonyl halide to produce the
bis(fluoroalkylenesulfonyl)imide as shown in Scheme 2.

Scheme 2

5    $2 \ Z-R_fSO_2X + NH_3 + 3 \ B \Rightarrow (Z-R_fSO_2)_2N^- \cdot BH^+ + 2B \cdot HX$,

when sulfonamides are used as the starting
compounds in the preparation of
bis(fluoroalkylenesulfonyl)imides according the method
of this invention, either the sulfonamide *per se*, or a

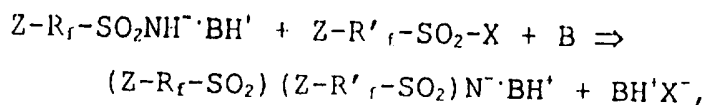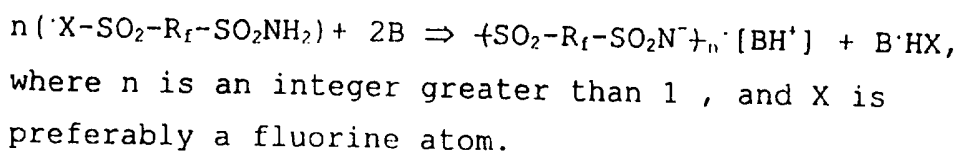10   salt of the sulfonamide may be used. As used herein,
the term "sulfonamide" represents both the sulfonamides
and the salts thereof. Thus, the use of
fluoroalkylenesulfonamide salts may be represented in
Scheme 3.

15

Scheme 3

$Z-R_f-SO_2NH^- \cdot BH^+ + Z-R'_f-SO_2-X + B \Rightarrow$

$(Z-R_f-SO_2)(Z-R'_f-SO_2)N^- \cdot BH^+ + BH'X^-$,

In another aspect of the invention, polymeric

20   bis(fluoroalkylenesulfonyl)imides may be prepared by
contacting equimolar amounts of difunctional
fluoroalkylene sulfonyl halides and fluoroalkylene
sulfonamides in the presence of a non-nucleophilic
base. The difunctional sulfonyl halides or

25   sulfonamides may be fluoroalkylene disulfonyl halides
or fluoroalkylene disulfonamides. Alternatively, a
difunctional sulfonamidofluoroalkylenesulfonyl halide
may be used. The preparation of polymeric imides is
shown in Schemes 4-6.

30

Scheme 4

$n(X-SO_2-R_f-SO_2NH_2) + 2B \Rightarrow \{SO_2-R_f-SO_2N^-\}_n \cdot [BH^+] + B \cdot HX$,
where n is an integer greater than 1 , and X is
preferably a fluorine atom.

Scheme 5

$H_2NSO_2-R_f-SO_2NH_2$ + $X-SO_2-R'_f-SO_2-X$ + 4B $\Rightarrow$ $+SO_2-R_f-SO_2N^-$-
$SO_2-R'_f-SO_2N^-+_n \cdot 2[BH']$ + $2B \cdot HX$.
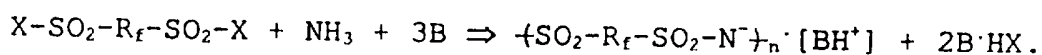
Scheme 6

$X-SO_2-R_f-SO_2-X$ + NH_3 + 3B $\Rightarrow$ $+SO_2-R_f-SO_2-N^-+_n \cdot [BH^+]$ + $2B \cdot HX$.
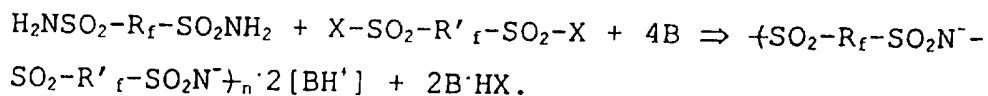
In Scheme 6, the sulfonamide is generated *in situ* by the reaction between a sulfonyl halide and ammonia in the presence of a non-nucleophilic base B. The sulfonamide thus produced reacts with a sulfonyl halide from another molecule of $X-SO_2-R_f-SO_2-X$ to produce the imide. Where sulfonamides are used as starting compounds, either the sulfonamide per se can be used, or a salt as previously described. Preferably $X-SO_2-R_f-SO_2-X$ is chosen so that the R_f group is sufficiently large to make intramolecular cyclization unfavorable. Cyclization would be unfavorable when the resulting cyclic compound would have a ring size ≤ four ring atoms or ≥ nine ring atoms.

In the preparation of polymeric imides according to Schemes 4-6 it is preferable that the reagents be of the highest possible purity (e.g., > 99% by weight) and have a high level of difunctionality (e.g., > 99%) so that the reaction proceeds to high levels of conversion (e.g., >98%) with minimal side reactions in order to maximize the molecular weight of the final polymer.
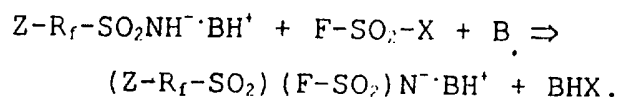
(Fluoroalkylsulfonyl)(fluorosulfonyl)imides can be prepared by the method of this invention using a fluoroalkylsulfonamide and a fluorosulfonyl halide according to Scheme 7.

Scheme 7

$$Z-R_f-SO_2NH_2 + F-SO_2-X + 2B \Rightarrow (Z-R_f-SO_2)(F-SO_2)N^-\cdot BH^+ +$$
BHX.
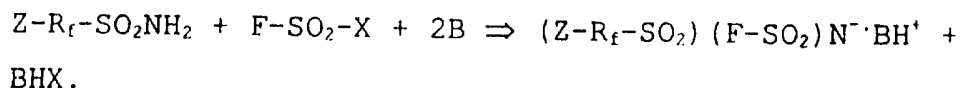
The fluoroalkylsulfonamide is preferably
5   generated *in situ* by the reaction between a
fluoroalkylsulfonyl halide and ammonia, and
subsequently reacted with the fluorosulfonyl halide to
produce the imides. As previously described, the
fluoroalkylsulfonamide per se may be used, or a salt as
10   shown in Scheme 8.

Scheme 8

$$Z-R_f-SO_2NH^-\cdot BH^+ + F-SO_2-X + B \Rightarrow$$
$$(Z-R_f-SO_2)(F-SO_2)N^-\cdot BH^+ + BHX.$$

15

Difunctional fluoroalkylenesulfonamides may
also be reacted with monofunctional
fluoroalkylenesulfonyl halides, or conversely,
difunctional fluoroalkylenesulfonyl halides may be
20   reacted with monofunctional fluoroalkylenesulfonamides
to produce dimeric bis(fluoroalkylenesulfonyl)imides,
as shown in Schemes 9 and 10.

Scheme 9

25   $$X-SO_2-R_f-SO_2X + 2 \ Z-R'_fSO_2NH_2 + 4B \Rightarrow Z-R'_fSO_2N^-SO2-Rf-SO_2N^-$$
$$-SO_2-R'_f-Z^-[2BH^+] + 2B\cdot HX$$

Scheme 10

$$H_2N-SO_2-R_f-SO_2NH_2 + 2 \ Z-R'_f-SO_2-X + 4B \Rightarrow Z-R'_fSO_2N^-SO2-Rf-$$
30   $$SO_2N^--SO_2-R'_f-Z^-[2BH^+] + 2B\cdot HX$$
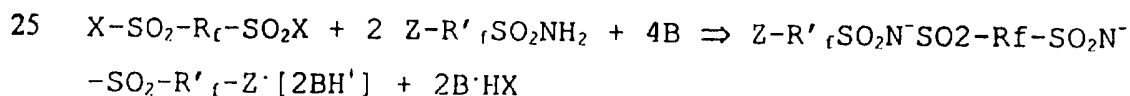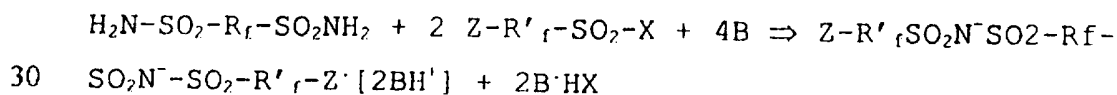
The fluoroalkylene groups, R_f and R_f', of the
fluoroalkylenesulfonyl halides and the
fluoroalkylenesulfonamides may be linear, branched,
35   cyclic or acyclic, or combinations thereof.

Additionally one or more of the fluorine or hydrogen
atoms of the fluoroalkylene group may be replaced by
chlorine or bromine atoms. In the above formulae shown
in Schemes 1 to 10, one or more non-adjacent carbon
5 atoms of the fluoroalkylene groups R_f and R'_f may be
replaced by catenary divalent oxygen or trivalent
nitrogen atoms.

When the fluoroalkylene group is acyclic it
has the general formula $C_mH_{(2m-a)}F_a$, where m is 1 to 12
10 and a is at least one. When the fluoroalkylene group
contains a cyclic group it has the general formula
$C_mH_{(2m-2-a)}F_a$, where m is 1 to 12 and a is at least one.
Preferably the sum of carbon atoms in the two
fluoroalkylene groups of the
15 bis(fluoroalkylenesulfonyl)imide is 3 to 12 carbon
atoms

Preferably, the fluoroalkylene group is
substantially fluorinated so that the number of
fluorine atoms is greater than the number of hydrogen
20 atoms present. Most preferably the fluoroalkylene
group is a linear or branched, cyclic or acyclic
perfluoroalkylene group containing 1 to 10 carbon atoms
and the sum of carbon atoms, in the two fluoroalkylene
groups of the bis(fluoroalkylenesulfonyl)imide is 3 to
25 12 carbon atoms.

The halide X may be F, Br or I, but is
preferably F. When Z is a polymerizable organic
functional group it allows the preparation of polymers
having pendant bis(fluoroalkylenesulfonyl)imide
30 moieties on the polymer chain.
Fluoroalkylenesulfonylfluorides having polymerizable
functional groups have been described by Gard et al.,
J. Fluorine Chem. 66, 105(1994), Gard et al.,
Coordination Chemistry Reviews 112, 47(1992), Gard et
35 al., J. Fluorine Chem. 49, 331(1990), Gard et al. J.

Fluorine Chem. 43, 329(1989), Gard et al., J. Fluorine Chem. 67, 27(1994), Gard et al. J. Fluorine Chem. 55, 313(1991), Gard et al. J. Fluorine Chem. 38, 3(1988), Gard et al., Inorg. Chem., 29, 4588(1990) U.S.

5   5,414,117 (Armand) and U.S. 5,463,005 (Desmarteau). Polymers prepared from fluoroalkylenesulfonylfluorides having polymerizable functional groups have been described in DesMarteau, Novel Fluorinated Acids for Phosphoric Acid Fuel Cells, Gas Research Institute

10   Report #GRI-92/0385, July 1992, and J. Fluorine Chem. 72,203 (1995).

Z may be any organic functional group that may undergo grafting or polymerization by an addition or step-growth mechanism, including cationic, anionic,

15   free-radical and Z-N polymerization or polycondensation. Z may be chosen from those groups containing double bonds, for example vinyl, allyl, vinyl-benzyl or acryloyl groups. Z may also be chosen from those groups containing oxirane, oxetane,

20   azetidine, or aziridine functional groups. Z may also be chosen from those groups containing alcohol, amine, isocyanate, or trialkoxysilyl functional groups.

When Z contains functional groups whose reactivity could interfere with reactions for preparing

25   the imides, Z can be protected by reactants that are reversibly bound to it. For example, a double bond may be protected as a di-halo derivative and subsequently dehalogenated. Examples of Z include $CH_2=CH-$, $CH_2=CHO-$, $CH_2=CHCH_2O-$, $CH_2=CHCO-$, $(CH_2=CHCH_2)_2NCO-$ (prepared as

30   described in Armand et.al, US 5,414,117), $(CH_2=CHCH_2)_2NSO_2-$ $CF_2=CFO-$, $CF_2=CF-$, $CH_2=CHCO_2CH_2CH_2-$, $-O-C_6H_4-CH=CH_2$, $-C(O)OCH_2CH_2OC(O)C(CH_3)=CH_2$, $-C(O)NCH_2CH_2OC(O)C(CH_3)=CH_2$, $-SO_2O-C_6H_4-CH=CH_2$, $-OCH_2CHOH-CH_2OH$, $-C(O)C(CH_3)=CH_2$, $-C(O)OCH_2CH=CH_2$, and $-OCH_2C\equiv CH$.

Perfluoroalkylsulfonyl fluorides and perfluoroalkylenedisulfonyl fluorides used as precursors to the imide salts of this invention can be prepared by a variety of methods known in the art as

5   described, for example, in U.S. Patents 3,542,864; 5,318,674; 3,423,299; 3,476,753, 3,776,960, 2,519,983, 3,951,762; 3,623,963; 2,732,398 S. Temple, J.Org. Chem., 33(1), 344 (1968), D.D. DesMarteau, Inorg. Chem., 32, 5007 (1993), and Chemistry of Organic

10   Fluorine Compounds, M. Hudlicky, ed., 2nd ed. PTR Prentice Hall (New York), pp. 73-6.

Perfluoroalkylsulfonyl fluorides are available by the electrochemical fluorination of the corresponding alkylsulfonyl· fluorides as described in

15   U.S. 2,732,398 (Brice et al.). See also T. Abe et al., in Preparation, Properties and Industrial Applications of Organofluorine Compounds, R.E. Banks(Ed), pages 37-9, John Wiley & Sons, New York (1982). Routes to perfluoroalkanesulfonyl chlorides are described by P.J.

20   Stag et al. in Synthesis 1982, 85 and by R.N. Haszeldine et al., in J. Chem. Soc. 1955, 2901. The chlorides of ω-hydrofluorinated sulfonic acids are described by Coffman and Raasch in J. Org. Chem,. 14, 747 (1949), by Weiyuan et al. in Chemistry 2, 31

25   (1987), and by Huang, J. Fluorine Chem. 32, 179 (1986).

Ammonia, when used in the method of this invention, should be anhydrous to prevent side reactions from occurring. To avoid the hazards of handling liquid ammonia, it is often convenient to

30   generated anhydrous ammonia in situ by reacting ammonium salts of the formula $NH_4{}^+X^-$ with one equivalent of a non-nucleophilic base. Here X may be any halide, or any other non-reactive anion.

For purposes of this description, the term

35   "non-nucleophilic base" B means a base which does not

undergo an irreversible reaction with the sulfonyl
halide group. This reaction, when it occurs will
reduce the yields of the desired imide. The non-
nucleophilic base may be an organic or inorganic base,
5   but is preferably an organic aprotic base. Examples of
suitable organic   non-nucleophilic bases include
alkylamines, for example triethyl amine, trimethyl
amine, tripropyl amine and diisopropylethyl amine,
pyridines, alkyl pyridines and dialkylaminopyridines,
10 alkyl piperadines, dialkyl piperazines, N-alkyl
pyrrolidines, N-alkylpyrroles N-alkylimidazoles,
amidines, for example 1,5-diazabicyclo[4.3.0]non-5-ene
(DBN) or 1,8-diazabicyclo[5.4.0]dec-7-ene (DBU), or
guanidines.   .

15   It is preferable to prepare the
bis(fluoroalkylenesulfonyl)imides neat, i.e. in the
absence of any solvent. Generally a solvent is not
necessary, the reactants are sufficiently soluble in
each other to produce the imides. In some cases,
20 solvents may be added to enhance the solubility of the
reactants, such as when preparing polymeric imides from
difunctional sulfonyl halides and/or sulfonamides. Any
solvent that is non-reactive toward the starting
sulfonyl halides and sulfonamides may be used, but
25 polar aprotic solvents are preferred. Any solvent used
should be anhydrous, (e.g., less than 1% water) to
avoid competing hydrolysis of the sulfonyl halides.
Examples of suitable aprotic liquids include linear
ethers such as diethyl ether, diethylene glycol
30 dimethyl ether, and 1,2-dimethoxyethane; cyclic ethers
such as tetrahydrofuran, 2-methyltetrahydrofuran,
dioxane, dioxolane, and 4-methyldioxolane; nitriles
such as acetonitrile and benzonitrile; nitro compounds
such as nitromethane or nitrobenzene; amides such as
35 N,N-dimethylformamide, N,N-diethylformamide, and N-

methylpyrrolidinone; sulfoxides such as dimethyl
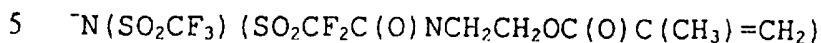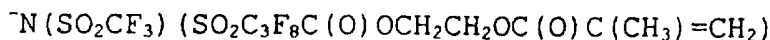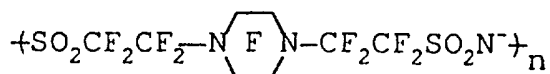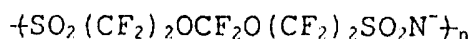sulfoxide; sulfones such as dimethylsulfone,
tetramethylene sulfone, and other sulfolanes;
oxazolidinones such as N-methyl-2-oxazolidinone and

5   mixtures thereof.

The method of this invention can be carried
out by introducing the reactants into a vessel, which
can be made of glass or other corrosion-resistant
material. Preferably the vessel is suitable for use at

10   elevated pressures caused by the high vapor pressure(s)
of certain reagents (e.g., NH₃). The method of this
invention can generally by carried out by heating the
contents of the vessel at temperatures from about -25°C
to about 150°C, preferably from 25°C to about 100°C and

15   at a pressure equal to or greater than atmospheric.
Generally pressures in excess of those generated by the
vapor pressures of the reagents at the reaction
temperatures is not required.

When preparing non-polymeric imides from

20   fluoroalkylsulfonamides generally at least one molar
equivalent of the sulfonyl halide is used. Preferably
a slight stoichiometric excess of the sulfonyl halide
is used. When preparing imides from ammonia, as shown
in Scheme 2, a stoichiometric excess of sulfonyl

25   halide, relative to the amount of ammonia, is generally
preferred. The amount of non-nucleophilic base used is
generally in excess of the stoichiometric amount shown
in Schemes 1 through 6. Preferably the amount of base
is less than a 100% excess of the stoichiometric amount

30   shown in the Schemes. Most preferably amount of base
is less than a 50% excess of the stoichiometric amount
shown in the Schemes to maximize the volume efficiency
of the reaction.

Representative imides that can be prepared by

35   the method of this invention include:

$^-N(SO_2CF_3)_2$ $^-N(SO_2C_2F_5)_2$ $^-N(SO_2C_4F_9)_2$

$^-N(SO_2C_8F_{17})_2$ $^-N(SO_2CF_2CF_2CFClCF_2Cl)_2$

$^-N(SO_2CF_2-c-C_6F_{11})_2$ $^-N(SO_2CF_2CF_2OCFClCF_2Cl)_2$

$^-N(SO_2C_3F_6CF_2Cl)_2$ $^-N(SO_2C_3F_6CF_2H)_2$ $^-N(SO_2C_2F_4N(CF_3)_2)_2$

$^-N(SO_2CF_2CF_2OCF=CF_2)_2$ $^-N(SO_2CF_2CF_2OCF_3)_2$ $^-N(SO_2CF_2CF_2CF=CF_2)_2$

$^-N(SO_2C_4F_8OCH=CH_2)_2$ $^-N(SO_2C_2F_4OCH_2CH=CH_2)_2$ $^-N(SO_2CF_3)(SO_2C_2F_5)$

$^-N(SO_2CF_3)(SO_2C_4F_9)$ $^-N(SO_2CF_3)(SO_2C_8F_{17})$ $^-N(SO_2C_2F_5)(SO_2C_4F_9)$

$^-N(SO_2CF_3)(SO_2F)$ $^-N(SO_2C_4F_9)(SO_2F)$ $^-N(SO_2CF_3)(SO_2CF_2H)$

$^-N(SO_2CF_3)(SO_2C_2F_4N(CF_3)_2)_2$ $^-N(SO_2CF_3)(SO_2C_2F_4CFClCF_2Cl)$

$^-N(SO_2CF_3)(SO2C2F4OCFClCF2Cl)$ $^-N(SO_2CF_3)(SO_2C_2F_4OCF=CF_2)$

$^-N(SO_2CF_3)(SO_2C_2F_4OCF_3)$ $^-N(SO_2CF_3)(SO_2C_2F_4CF=CF_2)$

$^-N(SO_2CF_3)(SO_2C_2F_4OCH_2CH=CH_2)$ $^-N(SO_2CF_3)(SO_2C_3F_6CF_2H)$

$^-N(SO_2CF_3)(SO_2C_2F_4OC_3F_6OCF=CF_2)$ $^-N(SO_2CF_3)(SO_2C_4F_8OCH=CH_2)$

$^-N(SO_2CF_3)(SO_2C_2F_4OC_2F_4CH=CH_2)$ $^-N(SO_2CF_3)(SO_2C_2F_4CON(CH_2CH=CH_2)_2)$

$^-N(SO_2CF_3)(SO_2C_2F_4OCH_2CHOHCH_2OH)$ $^-N(SO_2CF_3)(SO_2C_2F_4COC(CH_3)=CH_2)$

$^-N(SO_2CF_3)(SO_2CF_2C(O)OCH_2CH=CH_2)$ $^-N(SO_2CF_3)(SO_2C_2F_4OCH_2C=CH)$

$CF_3SO_2N^-SO_2C_4F_8SO_2N^-SO_2CF_3$ $C_2F_5SO_2N^-SO_2(CF_2)_6SO_2N^-SO_2C_2F_5$

$^-N(SO_2C_2F_4OC_2F_4CH=CH_2)_2$ $^-N(SO_2CF_2C(O)N(CH_2CH=CH_2)_2)_2$

$^-N(SO_2CF_2CF_2OCH_2\!-\!\langle C_6H_4 \rangle\!-\!CH=CH_2)_2$ $N^-(SO_2CF_2CF_2-N\langle F \rangle O)_2$

$^-N(SO_2CF_3)(SO_2CF_2CF_2OCH_2-CH\!-\!CH_2\ \text{(epoxide)})$ $^-N(SO_2CF_3)\ SO_2CF_2CF_2-N\langle F \rangle O$

$^-N(SO_2C_3F_6SO_2N(CH_2CH=CH_2)_2)_2$

$$CF_3N\!\!\begin{array}{c}\diagup C_2F_4SO_2N^-SO_2CF_3 \\ \diagdown C_2F_4SO_2N^-SO_2CF_3\end{array}$$

$$CF_3SO_2N^-SO_2CF_2CF_2\!\!-\!\!N\langle F \rangle N\!\!-\!\!CF_2CF_2SO_2N^-SO_2CF_3$$

$CF_3SO_2N^-SO_2CF_2CF_2OCH_2CH_2OCF_2CF_2SO_2N^-SO_2CF_3$

5    $CH_2=CHCH_2OC_2F_4SO_2N^-SO_2(CF_2)_4SO_2N^-SO_2C_2F_4OCH_2CH=CH_2$

$+SO_2CF_2CF_2N(CF_3)CF_2CF_2SO_2N^-SO_2(CF_2)_6SO_2N^-+_n$

$+SO_2(CF_2)_3SO_2N^-SO_2(CF_2)_4SO_2N^-+_n$

$+SO_2(CF_2)_2OCH_2CH_2O(CF_2)_2SO_2N^-+_n$

$$+SO_2CF_2SO_2N^-SO_2(CF_2)_nSO_2N^-\!+_n$$

$$+SO_2(CF_2)_2OCF_2O(CF_2)_2SO_2N^-\!+_n$$

$$+SO_2CF_2CF_2-N\!\!\bigcirc\!\!F\bigcirc\!N-CF_2CF_2SO_2N^-\!+_n$$

$$^-N(SO_2CF_3)(SO_2C_3F_8C(O)OCH_2CH_2OC(O)C(CH_3)=CH_2)$$

5   $^-N(SO_2CF_3)(SO_2CF_2C(O)NCH_2CH_2OC(O)C(CH_3)=CH_2)$

$$^-N(SO_2C_2F_5)(SO_2C_3F_6SO_2N(CH_2CH=CH_2)_2)$$

     The imides shown (without a corresponding
cation for illustrative purposes) can be used to
10   prepare derivatives such as alkali, alkaline earth and
other metal salts, N-silyl imides, N-alkyl and N-fluoro
imides. For example, conjugate acids of the imides
may be treated with an inorganic base having the
desired cation M', such as NaOH, LiOH, KOH, NH₄OH, Ag₂CO₃
15   or CuO, to produce the corresponding N-Na, N-Li, N-K,
N-NH₄, N-Ag or N-Cu salts. The imides may be contacted
with fluorine under direct fluorination conditions to
produce the N-F derivatives. The silver imide salts
may be contacted with a trialkylsilyl chloride,
20   trialkylstannyl chloride, or an alkyl halide to produce
the N-trialkylsilyl, N-trialkylstannyl or N-alkyl
derivatives respectively. Other derivatives can be
prepared by means known to those skilled in the art.
     The invention is further illustrated by the
25   following Examples. In the examples, the term "reduced
pressure" means the vacuum obtained by means of a
commercially available laboratory distillation
apparatus using an aspirator connected to a water pipe
or other fluid stream for aspiration, such as a rotary
30   evaporator apparatus.

<u>Example 1</u>

Lithium(trifluoromethanesulfonyl)

(perfluorobutanesulfonyl)imide

Under a nitrogen atmosphere, a dry, 500 mL
Fisher-Porter pressure bottle equipped with a stainless
5   steel pressure head and magnetic stirrer was charged
with 35.00 g $CF_3SO_2NH_2$ (prepared, e.g., as described in
Foropoulos and DesMarteau, Inorg. Chem., 23:3720-23
(1984)), 98 mL anhydrous triethylamine and 74.55 g
$C_4F_9SO_2F$. The pressure vessel was sealed and the
10   reaction mixture heated to 90°C with stirring for 17
hours. The volatile components of the reaction mixture
were evaporated under reduced pressure at 70°C then the
reaction mixture was treated with a mixture of 700 mL
water and 700 mL methylene chloride with stirring to
15   form a two phase mixture. The methylene chloride phase
was then separated, washed with two 700 mL portions of
water, dried over anhydrous $MgSO_4$, filtered and then
evaporated under reduced pressure to yield a dark red
liquid. This liquid was combined with 500 g of
20   polyphosphoric acid (Aldrich Chemical Co.) in a short
path vacuum distillation apparatus equipped with an
ambient air-cooled condenser, and then vacuum distilled
at ca. 0.1 Torr. The distillate (96.5 g, corresponding
to $HN(SO_2CF_3)(SO_2C_4F_9)$, which solidified in receiver at
25   0°C, was further purified by sublimation at 70°C, 1.0
Torr and then added in portions to a slurry of 52 g of
Li_2CO_3 (99.997% purity, from Aldrich Chemical Co.) in
800 mL of methyl t-butyl ether with stirring at room
temperature. After about 1 hour CO_2 evolution subsided
30   and the reaction mixture was heated to about 40°C for
3.5 hours to complete the neutralization. The mixture
was filtered by gravity through filter paper and then
filtered again by suction through a 0.22 micron Tefsep®
Teflon membrane (Micron Separations Inc., Westboro,
35   Massachusetts) to remove particulates. The filtrate

was evaporated under reduced pressure at 25-80°C to
yield a clear, colorless oil. Two 250 mL portions of
toluene were combined with the oil and the mixture
evaporated at 40-70°C, 20 Torr after each toluene

5   addition, causing the oil to eventually solidify giving
a fine white powder. The solid was transferred to a
glass jar and dried in vacuo at 100°C, 10^{-2} Torr for 24
hours to yield 77.0 g of the anhydrous title salt. The
structure of the product was confirmed by ^{1}H and ^{19}F NMR

10   spectroscopy which indicated that the purity of the
salt was greater than 99% by weight.

                          Example 2
       Lithium (trifluoromethanesulfonyl)

15   (perfluoroethanesulfonyl)imide

               Under a nitrogen atmosphere, a dry 3L flask
       equipped with a dry ice condenser, mechanical stirrer,
       and a sparging tube was charged with 500 mL anhydrous

20   methyl t-butyl ether (MTBE) and cooled below 0°C in a
       dry ice bath. To the cold solvent was added 500 g of
       crude $CF_3CF_2SO_2F$ mixture (containing ca. 23% $CF_3CF_2SO_2F$
       by weight in C6-C8 perfluoroalkane solvent). Gaseous
       anhydrous ammonia (194 g) was gradually introduced

25   through the sparging tube into the resulting mixture at
       ca. 0°C with vigorous stirring. Once ammonia addition
       was complete, the reaction was allowed to proceed for
       an additional hour after which the dry ice bath was
       removed and the reaction solution gradually warmed to

30   room temperature with stirring. Excess ammonia was
       allowed to evaporate while stirring overnight at room
       temperature. The reaction solution was cooled again to
       0°C and treated with 83.9 g LiOH·H₂O dissolved in 750 mL
       of water with stirring. The mixture was filtered

35   through filter paper by gravity to remove LiF

precipitate. To the filtrate was added concentrated aqueous HCl in portions with stirring at 0°C until the pH of the mixture was 0.

5   The resulting two-phase mixture was separated into separate aqueous and ether phases. The aqueous phase was extracted with two additional 400 mL portions of MTBE. The ether fractions were combined, extracted with two 500 mL portions of water, and then dried over anhydrous $MgSO_4$ overnight. The ether solution was

10   filtered by gravity through filter paper and then by suction through a 0.22 micron Tefsep™ membrane (Micron Separations Inc.). The filtrate was concentrated by rotary evaporation, hexane was added, and the solution concentrated again. This was repeated until the

15   product $CF_3CF_2SO_2NH_2$ crystallized from solution as a white solid. The product (Crop 1) was isolated by suction filtration through a glass frit giving 33.0 g. A second crop of crystals (20.2 g) was recovered in the same manner from the filtrate by concentrating further

20   followed by filtration. The remaining filtrate was evaporated to dryness at 40°C , 20 torr to yield a third crop of relatively crude product (26.8 g). All product fractions (Crops 1-3) were dried at 10^{-2} torr at room temperature for ca. 15 min to give a combined yield of

25   80.0 g. Quantitative ^1H and ^{13}C NMR analysis of the product from Crop 2 indicated that it was the desired product with a purity of 98% by weight.

      Under a nitrogen atmosphere, a dry Parr 4560-Series Benchtop Mini Reactor equipped with a 600 mL

30   capacity Monel reactor cylinder, mechanical stirrer, thermocouple and heating mantle was charged with 53 g $CF_3CF_2SO_2NH_2$ (Crops 1 + 2) and 152 mL anhydrous triethylamine. While cooling the reactor at -78°C in dry ice, 55.2 g of gaseous CF_3SO_2F (ca. 94% purity) was

35   condensed into the reactor with stirring. The reactor

was sealed and the temperature of the reaction mixture
gradually raised to 90°C with vigorous stirring, then
held at 90°C with stirring for a total of 24 hours. The
volatile components of the reaction mixture were

5   evaporated under reduced pressure at 70°C, then the
residue was treated with a mixture of 700 mL water and
700 mL methylene chloride with stirring to form a two
phase mixture. The methylene chloride phase was then
separated, washed with two 700 mL portions of water,

10   dried over anhydrous MgSO₄, filtered and then evaporated
under reduced pressure to yield a dark red liquid.
This liquid was combined with 600 g of polyphosphoric
acid (Aldrich Chemical Co.) in a short path vacuum
distillation apparatus equipped with an ambient air-

15   cooled condenser, and then vacuum distilled at ca. 15
torr, 85-88°C. The distillate (78.1 g, corresponding to
HN(SO₂CF₃)(SO₂C₂F₅)), which solidified in receiver at
0°C, was converted to the corresponding lithium salt,
and further purified, using essentially the procedure

20   described in Example 1 to yield 75.0 g of the anhydrous
title salt. The structure of the product was confirmed
by ¹H and ¹⁹F NMR spectroscopy which indicated that the
purity of the salt was 98% by weight.

Example 3

Lithium Bis(perfluoroethanesulfonyl)imide

5   As in Example 2, a dry Parr 4560-Series
Benchtop Mini Reactor was charged with 155 mL anhydrous
triethylamine. While cooling the reactor at -78°C in
dry ice, gaseous $C_2F_5SO_2F$ (100.0 g, > 99% purity)
followed by anhydrous ammonia (3.51 g) were condensed
10   into the reactor with stirring. The reactor was sealed
and the temperature of the reaction mixture gradually
raised to 90°C with vigorous stirring. The reaction
mixture was held at 90°C with stirring for a total of
20.5 hours. The intermediate product, $HN(SO_2C_2F_5)_2$, was
15   isolated as previously described, then added to a
slurry of Li_2CO_3 (45.7 g, 99.997% purity) in 800 mL of
methyl t-butyl ether to produce the lithium salt. This
lithium salt was isolated using essentially the
procedure described in Example 1 to yield 73.34 g (92%
20   yield based upon NH_3) of the anhydrous title salt. The
structure of the product was confirmed by ^1H and ^{19}F NMR
spectroscopy which indicated that the purity of the
salt was 99.9% by weight.

25   Example 4
Lithium Bis(perfluorobutanesulfonyl)imide

          As in Example 1, a dry, 500 mL Fisher-Porter
pressure bottle was charged with anhydrous
30   triethylamine (100.5 g) and $C_4F_9SO_2F$ (145.0 g). The
pressure vessel was sealed, cooled to -78°C in dry ice
and then charged with of anhydrous ammonia (3.0 g) with
stirring. After warming gradually to room temperature,
the reaction mixture was heated to 90°C with stirring
35   for 24 hours. The intermediate product, $HN(SO_2C_4F_9)_2$,

was isolated as previously described, then added to a
slurry of Li$_2$CO$_3$ (40.0 g, 99.997% purity) in 800 mL of
methyl t-butyl ether to produce the lithium salt. This
lithium salt was isolated using essentially the

5   procedure described in Example 1 to yield 90.8 g (86%
yield based upon NH$_3$) of the anhydrous title salt. The
structure of the product was confirmed by ^{1}H and ^{19}F NMR
spectroscopy which indicated that the purity of the
salt was 98% by weight.

10

Example 5

Lithium Bis(perfluoropropanesulfonyl)imide

As in Example 4, the title compound was

15   prepared using anhydrous triethylamine (100.5 g),
C$_3$F$_7$SO$_2$F (100.0 g, 68:32 iso:normal isomer ratio), and
anhydrous ammonia (3.0 g). A total of 40.8 g of the
anhydrous title salt was recovered as a light pink
solid. Quantitative analysis by ^{1}H and ^{19}F NMR

20   spectroscopy indicated that the product contained the
following major components in order of decreasing
weight percent: Li$^+$ $^-$N(SO$_2$C$_3$F$_7$)$_2$, 85.1%, 39:61 iso:normal
C$_3$F$_7$ ratio; Li$^+$ $^-$N(SO$_2$i-C$_3$F$_7$)(SO$_2$F), 8.7%; Li$^+$ $^-$N(SO$_2$n-
C$_3$F$_7$)(SO$_2$F), 4.2%.

25

Example 6

Synthesis of Lithium trifluoromethylsulfonyl
perfluoro(dimethylaminoethylsulfonyl) imide
30   Li$^+$$^-$N(SO$_2CF_3$)(SO$_2C_2F_4$N(CF$_3$)$_2$)

The hydrocarbon precursor 2-
dimethylaminoethylsulfonylfluoride was made by the
addition of dimethylamine to vinylsulfonyl fluoride as

35   described in Krutak et al., J. Org. Chem., 44(2):3847-
58 (1979). The hydrocarbon was perfluorinated by
electrochemical fluorination. An electrochemical cell

of the type described in U.S. Patent No. 2,519,983
(Simons) was filled with 1500 cm³ anhydrous HF. The
cell was operated at 31 psig (214 Kpa) and at an
average temperature of 56°C. During the course of the

5 129 hour run, 456 grams of fluorinated product was
produced from 650 grams (4.2 mole) of starting
material. Analysis of the fluorocarbons was done using
gas chromatography/FTIR to confirm structures and
yields. The resulting fluorochemical was distilled in

10 a 3-plate distillation column to a main cut of 374
grams (1.1 moles, 27% molar yield) corresponding to
perfluorodimethylaminoethylsulfonyl fluoride
((CF₃)₂NC₂F₄SO₂F) .

To a dry flask equipped with a reflux

15 condenser and magnetic stirrer was charged 1.13 g
CF₃SO₂NH₂ (prepared, e.g., as described in Foropoulos
and DesMarteau, Inorg. Chem., 23:3720-23 (1984)), 20 ml
anhydrous triethylamine (distilled from LiAlH₄) and
2.67g (CF₃)₂NC₂F₄SO₂F. The reaction mixture was heated

20 to 70°C under a nitrogen atmosphere with stirring for 17
hours, after which volatile components were removed
under reduced pressure. The residue was treated with a
mixture of 40 mL water and 40 mL methylene chloride
with stirring to form a two phase mixture. The

25 methylene chloride phase was then separated, washed
with two 40 mL portions of fresh water to remove water-
soluble components, dried over anhydrous MgSO₄, filtered
and then evaporated under reduced pressure to yield a
dark red liquid. The liquid residue was combined with

30 20 mL of concentrated (at least 98 weight percent H₂SO₄)
sulfuric acid in a short path distillation apparatus
equipped with a dry-ice cooled condenser, and then
vacuum distilled at 10⁻¹ torr, 60°C. The distillate was
dissolved in 50 mL of diethyl ether, after which the

35 resulting ether solution was treated with excess

-20-

lithium carbonate for 2 hours with stirring at room
temperature, filtered and the filtrate evaporated under
reduced pressure to yield a clear, colorless oil.
Approximately 100 mL of toluene were combined with the

5   oil and the mixture evaporated again at 40-70°C, 20
torr, causing the oil to solidify to form the title
salt.   The structure of ·the product was confirmed by ^{1}H
and ^{19}F NMR.

10   Example 7

Preparation of Dilithio perfluoro(methyl-bis-
trifluoromethylsulfonimidoethyl)amine
$CF_3N(CF_2CF_2SO_2N^-SO_2CF_3)_2 \cdot 2Li^+$

15
A 500 mL flask equipped with an addition
funnel and stir bar was charged with 10 g of $CF_3SO_2NH_2$,
45 mL of dry THF and 45 mL of dry triethylamine, then
cooled to 0"C under nitrogen. 15 g of $CF_3N(CF_2CF_2SO_2F)_2$

20   (prepared by electrochemical fluorination of
$CH_3N(CH_2CH_2SO_2F)_2$) was then added slowly to the stirred
solution. After complete addition, the reaction was
allowed to warm to room temperature and stirred for an
additional 92 hours. Next, the mixture was evaporated

25   to a brown oil under reduced pressure, which was then
dissolved in 300 mL of aqueous 1M LiOH. The water,
triethylamine and other volatile components were then
evaporated under reduced pressure and the remaining
solid washed with 100 mL of diethyl ether. The ether

30   solution was filtered, then evaporated under reduced
pressure to yield a brown oil, which was dissolved in a
small amount (quantity just sufficient to dissolve the
oil) of diethyl ether, then added to 100 mL of
methylene chloride. This solution was again filtered

35   and evaporated to yield 3.5 g of a yellow solid
corresponding to the title salt. The structure was
confirmed by ^{1}H and ^{19}F NMR.

Example 8

Preparation of Lithium bis-
perfluoro(dimethylaminoethyl)sulfonimide
Li$^+$ $^-$N(SO$_2$C$_2$F$_4$N(CF$_3$)$_2$)$_2$

A 500 mL Fisher-Porter pressure bottle,
equipped with a magnetic stir bar and pressure head,
was charged with 30 g of (CF$_3$)$_2$NC$_2$F$_4$SO$_2$NH$_2$ (prepared by
treatment of (CF$_3$)$_2$NC$_2$F$_4$SO$_2$F (prepared by electrochemical
fluorination of (CH$_3$)$_2$NC$_2$H$_4$SO$_2$F)) with excess ammonia in
tetrahydrofuran), 27.4 g of triethylamine and 31.8 g of
(CF$_3$)$_2$NC$_2$F$_4$SO$_2$F. The flask was sealed and heated to
160°C for 37 hrs with stirring. After cooling, the
volatile components of the reaction mixture were
evaporated under reduced pressure. The residue was
dissolved in 300 mL of methylene chloride and extracted
three times with 300 ml of water each time. The
methylene chloride solution was then dried over MgSO$_4$,
filtered, and the solvent removed under reduced
pressure. The residue was then distilled from excess
polyphosphoric acid over a temperature and pressure
range starting from 105°C and 3 torr and ending at 97°C
and 0.2 torr to yield 40.13 g of a pale yellow-orange
liquid which solidified on standing. This solid,
corresponding to HN(SO$_2$C$_2$F$_4$N(CF$_3$)$_2$)$_2$, was dissolved in
300 mL of methyl t-butyl ether, after which 20.6 g of
Li$_2$CO$_3$ was added in small portions with stirring. After
stirring overnight, a small amount of additional Li$_2$CO$_3$
was added and heated briefly until the solution tested
neutral to pH paper premoistened with distilled water.
The mixture was cooled, filtered and the solvent
removed under reduced pressure. Further drying under
vacuum at 110°C yielded 33.5 g of a fine white powder
corresponding to the title salt. The structure of the
product was confirmed by FTIR, and ^{19}F and ^{1}H NMR.

Example 9

Synthesis of Lithium (trifluoromethylsulfonyl)
(allyloxyoctaflurobutylsulfonyl)imide

5    $(CH_2=CHCH_2OC_4F_8SO_2N(Li)SO_2CF_3)$

A 50 mL flask was charged with dry, distilled
triethylamine (15mL), dry acetonitrile (15 mL) and
$CF_3SO_2NH_2$ (6.75g, 0.0081 mole), purged with nitrogen,

10   and cooled to about 0°C in an ice bath.
$CH_2=CHCH_2OC_4F_8SO_2F$ (3.0g, 0.0082 mole, prepared
essentially as described in Gard et al., J. Fluorine
Chem., 49, 331(1990) from $FC(O)(CF_2)_3SO_2F$, which was
prepared as described in U.S. 4,425,199) was added

15   dropwise to the solution with stirring, and the
reaction mixture was allowed to come to room
temperature overnight.

The solvent from the resulting brown mixture
was removed under reduced pressure, and aqueous LiOH

20   (30mL of 1M) was added. The mixture was stirred until
neutralization was complete. The water was removed
under reduced pressure and the resulting oil was
dissolved in diethyl ether, then filtered to removed
excess LiOH.

25   To the ether solution was added methylene
chloride (25mL) and sulfuric acid (15mL of 2M). The
organic layer was separated, neutralized with excess
Li_2CO_3, filtered and the insoluble portion washed with
acetonitrile. The volatile components of the combined

30   filtrate solutions were removed under reduced pressure,
and the resulting brown oil slowly crystallized to
yield clear crystals of the title compound. The
structure was confirmed by ^1H and ^{19}F NMR. Yield 2.73g,
71%.

35

Example 10

Preparation of Lithium (trifluoromethylsulfonyl)
(fluorosulfonyl)imide, $CF_3SO_2NLiSO_2F$.

5   A dry, 3-necked flask equipped with a nitrogen
inlet, stir bar and dry-ice condensor was charged with
dry triethylamine (15mL)and cooled in a dry
ice/isopropanol bath. Sulfuryl fluoride SO_2F_2 (7.0g,
6.8mmole) was bubbled into the cooled triethylamine.
10 The reaction mixture was allowed to warm to -30°C,
followed by dropwise addition of a solution of
triethylamine(10mL), acetonitrile (10mL) and $CF_3SO_2NH_2$
(4.0g, 0.027 mole). The temperature was maintained for
an hour, allowed to warm to room temperature, and then
15 stirred overnight.

The solvent was removed from the brown
reaction mixture under reduced pressure. The remaining
brown oil was dissolved in methylene chloride (75mL)
and washed with water, followed by 3M H_2SO_4, then dried
20 over $MgSO_4$. The solvent was removed under reduced
pressure, and the crude product purified by Kugelrohr
distillation (80°C at 1 torr)to yield $CF_3SO_2NHSO_2F$ as a
clear oil. This imide was dissolved in methyl t-butyl
ether, neutralized with excess Li_2CO_3, filtered and the
25 solvent removed under reduced pressure to yield the
title compound. Yield 3.5g, 55%.

Example 11

Preparation of Lithium
30 (difluoromethylsulfonyl)(trifluoromethylsulfonyl)imide,
$(HCF_2SO_2)(CF_3SO_2)NLi$

Difluoromethylsulfonyl chloride (30g, 0.2
mole) was dissolved in diethyl ether (100 mL) and
cooled to 0°C. An excess of anhydrous NH_3 was added
35 until the conversion to the difluoromethylsulfonamide

was complete by gas chromatography/mass spectroscopy.
The ether solution was evaporated to yield a reddish
oil, from which a yellow crystalline solid
precipitated. The crystals were washed with diethyl
5   ether, dried and then washed with hot toluene to remove
yellow, oil impurities.

A mixture of the purified
difluoromethylsulfonamide (26.5g, 0.2 mole),
triethylamine (60.6g, 0.6 mole) and
10   trifluoromethylsulfonyl fluoride (85% pure, 39.5g, 0.26
mole)were charged into a stainless steel pressure
vessel and heated at 45°C for 24 hours. The lower phase
was separated from the upper triethylamine phase,
dissolved in methylene chloride, and washed with water.
15   The solvent was removed under reduced pressure to yield
$(HCF_2SO_2)(CF_3SO_2)N^-(Et)_3NH^+$ (38.9g, 0.11 mole, 55%)

This ammonium salt was acidified with
concentrated H_2SO_4 (20 g)and distilled at 100°C and 5
torr to yield $(HCF_2SO_2)(CF_3SO_2)NH$ (9.8 g). This imide
20   (15.3 g, 0.06 mole from two preparations) was treated
with $LiOH \cdot H_2O$ (2.5 g, 0.06 mole in 50 mL water). The
solution was filtered and dried in a convection oven
overnight at 100°C, Yield 14.1 g of $(HCF_2SO_2)(CF_2SO_2)N^-$
Li^+.

25

Example 12

Preparation of bis(trifluoromethylsulfonyl)imide

30   A stainless steel pressure vessel was charged
with triethylamine (328 g, 3.25 mole), sealed, and
cooled to 0 C. Trifluoromethylsulfonyl fluoride (103.4
g of 85% purity, 0.68 mole) was added to the vessel via
a gas inlet, followed by anhydrous ammonia (4.76 g,
35   0.28 mole). The mixture was heated at 65°C for 24

hours, cooled and the lower product phase decanted.
The upper triethylamine phase was extracted with
methylene chloride, then combined with the lower
product phase and washed with water to remove by-
5   product salts. The solvent was removed under reduced
pressure to yield the crude salt: $(CF_3SO_2)N^-NH(C_2H_5)_3^+$.
The salt was acidified with concentrated sulfuric acid
(250 g), then purified by vacuum distillation to yield
the title compound. Yield 64.6 g, b.p. 100°C at 5 torr.
10   This imide was dissolved in water (100 mL), then
treated with $LiOH \cdot H_2O$ (9.67 g, 0.23 mole). The solution
was filtered, then dried to a white crystalline product
in a convection oven at 100°C. Yield 64.9 g of lithium-
bis-(trifluoromethylsulfonyl)imide. The structure was
15   confirmed by ^{19}F NMR.

Example 13

Preparation of [$(-SO_2(CF_2)_4SO_2N^-SO_2(CF_2)_3SO_2N^-)$ •
20   $2(C_2H_5)_3NH^+]_n$ Polymer

The reagents $H_2NSO_2(CF_2)_4SO_2NH_2$ (1.995 g, 5.539
mmoles; prepared by electrochemical fluorination of
$FSO_2(CH_2)_4SO_2F$ followed by amidation), $FSO_2(CF_2)_3SO_2F$
25   (1.751 g, 5.539 mmoles; prepared by electrochemical
fluorination of $FSO_2(CH_2)_3SO_2F$), triethylamine (3.363 g,
33.23 mmoles. dried over activated 3A molecular sieves)
and anhydrous acetonitrile (5 mL) were combined in a
dry 2 oz (~59.1 mL) jar equipped with a magnetic stir
30   bar and a tight-fitting cap to prevent significant
exposure to ambient moisture. Once all reagents were
fully dissolved, the contents were heated in an oil
bath at 65°C with stirring overnight. The temperature
was then increased to 75"C for 8 hours after which the
35   reaction solution was allowed to cool to room

temperature. Volatile components of the reaction
mixture were removed under vacuum at 70°C. The remaining
viscous residue was combined with a mixture of
methylene chloride and water and agitated in a
5   separatory funnel to extract by-product salts into the
aqueous phase. The polymeric product was only
partially soluble in the methylene chloride phase, the
remainder separated out as a third viscous brown oil
phase. The water fraction was separated and discarded,
10   and the remaining two organic fractions were extracted
an additional two times with water. The isolated
organic fractions were concentrated under vacuum at 80°C
to remove solvent and any other volatile components. A
brown viscous residue was obtained weighing 2.2 grams.
15   ^{1}H, ^{19}F and FTIR spectroscopic analysis identified the
product as the desired title polymer. Gel permeation
chromatographic analysis in methyl ethyl ketone
revealed a bimodal molecular weight(MW) distribution in
which 59% of the product had a number average MW of
20   19,670 (P.I. = 1.09) and 41% of the product had a
number average MW of 4,240 (P.I. = 1.12). End group
analysis by ^{19}F NMR indicated that the overall number
average MW was 1,860 and that the polymer chains were
terminated with sulfonamide and sulfonate end groups.
25   The lower than expected MW is attributed to partial
hydrolysis of the sulfonyl fluoride groups by trace
amounts of water in the reaction mixture.

The method shown in the Examples uses
relatively inexpensive reagents and provides high
30   yields of imides in a single step, i.e. without the
isolation of intermediate reaction products.
Furthermore, the method allows unsymmetrical imides
(imides having two different fluoroalkyl sulfonyl
groups, or fluorosulfonyl groups) to be prepared. The
35   method also allows the preparation of polymeric imides

from imides having a polymerizable functional group.
The imides prepared using the method of this invention
may be used, for example, as electrolytes in fuel cells
and batteries and as catalysts for polymerization and
5   esterification.

What is claimed is:

1.   A process for preparing an imide salt
selected from bis(fluoroalkylsulfonyl)imide

5   and(fluoroalkylsulfonyl)(fluorosulfonyl)imide salts
comprising the step of contacting a
fluoroalkylsulfonamide with a sulfonyl halide selected
from the group consisting of fluoroalkylsulfonyl
halides and fluorosulfonyl halides in the presence of a

10   sufficient amount of a non-nucleophilic base at a
temperature and for a time sufficient to yield the
imide salt.

2.   The process of Claim 1 wherein the

15   fluoroalkylsulfonamide is prepared by contacting a
fluoroalkylsulfonyl salt with anhydrous ammonia.

3.   The process of Claim 2 wherein the anhydrous
ammonia is generated *in situ* by the reaction of an

20   ammonium halide ($NH_4{}^+X^-$) with a non-nucleophilic base.

4.   The process of Claim 2 where the temperature
is from -25°C to 150°C.

25   5.   The process of Claim 1 characterized by the
reaction scheme:

$Z-R_f-SO_2NH_2 + Z-R'_f-SO_2-X + 2B \Rightarrow (Z-R_f-SO_2)(Z-R'_f-SO_2)N^-$
$\cdot BH^+ + BHX$,
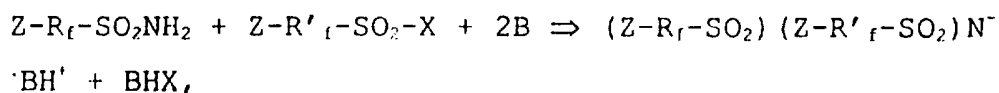
where each Z is a fluorine atom or a polymerizable

30   organic functional group, R_f and R'_f are fluoroalkylene
groups optionally containing catenary oxygen or
nitrogen, X is a halogen atom, and B is a non-
nucleophilic base.

6.   The process of Claim 5 wherein either or both of R_f and R'_f are perfluoroalkylene groups of the formula $-C_mF_{2m}-$, where m is 1 to 12.

5   7.   The process Claim 5 further comprising the step of isolating the bis(fluoroalkylsulfonyl)imide salts of the formula $(Z-R_f-SO_2)(Z-R'_f-SO_2)N^-\cdot BH^+$ by evaporating the volatile reaction product components, extracting the remaining reaction product in water and
10   methylene chloride, drying and filtering the methylene chloride phase, and removing residual solvent to yield a concentrated reaction product and acidifying by contacting the concentrated reaction product with a mineral acid to produce a bis(fluoroalkylsulfonyl)imide
15   of the formula $(Z-R_f-SO_2)(Z-R'_f-SO_2)N^-\cdot H^+$.

8.   The process of Claim 1 wherein the non-nucleophilic base is an organic base selected from the group of trialkylamines, alkyl aryl amines, and
20   pyridines.

9.   The process of Claim 1 further comprising contacting the bis(fluoroalkylsulfonyl)imide salt with an inorganic base having an alkali metal cation M^+,
25   volatilizing the non-nucleophilic base, and isolating the resulting bis(fluoroalkylsulfonyl)imide salt by filtration, evaporating volatile components from the residue, followed by solvent extraction of the filtrate and removal of the solvent.
30

10.   A process for the preparation of bis(fluoroalkylsulfonyl)imides comprising the step of contacting at least two equivalents of a fluoroalkylsulfonyl halide with one equivalent of
35   ammonia and at least three equivalents of a non-

nucleophilic base at a temperature and for a time
sufficient to yield the imide salt.

11. A process for preparing a
5   bis(fluoroalkylsulfonyl)imide which comprises
contacting a sulfonamidofluoroalkylenesulfonyl halide
of the formula $X-SO_2-R_f-SO_2NH_2$ with a non-nucleophilic
base at a temperature and for a time sufficient to
produce a polymeric fluoroalkylsulfonimide having the
10   repeat unit $+SO_2-R_f-SO_2N^-+_n$, wherein n is an integer
greater than 1 and X is a halogen atom.

12. A process for preparing a polymeric
fluoroalkylsulfonimide characterized by the reaction
15   scheme:

$H_2NSO_2-R_f-SO_2NH_2$ + $X-SO_2-R'_f-SO_2-X$ + 4B $\Rightarrow$ $+SO_2-R_f-SO_2N^--$
$SO_2-R'_f-N^-+_n$ 2BH⁺ 2B·HX, wherein n is an integer greater
than 1 and X is a halogen atom.

20   13. A process for preparing a polymeric
fluoroalkylsulfonimide characterized by the reaction
scheme:

$X-SO_2-R_f-SO_2-X$ + NH_3 + 3B $\Rightarrow$ $+SO_2-R_f-SO_2-N^-+_n$ + 2B·HX,
wherein n is an integer greater than 1, R_f is a
25   fluoroalkylene group, B is a non-nucleophilic base and
X is a halogen atom.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C303/38   C07C311/48

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)
IPC 6   C07C

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 256 821 A (M. ARMAND) 26 October 1993 see the whole document ---	1
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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

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Date of the actual completion of the international search	Date of mailing of the international search report
27 February 1997	0 7. 03. 97

| Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016 | Authorized officer

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