Title: PREPARATION OF COMPOUNDS WITH A PERFLUOROALKYL-SULFONYL GROUP

Abstract: Sulfuryl fluoride is reacted with a perfluoroalkene continuously, for example, under a pressure of up to 2 bars (abs), to form a sulfonyl fluoride or a sulfone. A preferred perfluoroalkene is hexafluoropropene which can be reacted with sulfuryl fluoride to form perfluoroisopropylsulfonyl fluoride.
Preparation of compounds with a perfluoroalkylsulfonyl group

The invention concerns a process for the preparation of compounds with a perfluoroalkylsulfonyl group by the addition of sulfuryl fluoride to perfluoroalkenes.

Sulfonyl fluorides are intermediates in chemical synthesis. For example, by hydrolysis with an aqueous base and subsequent acid treatment, they can be converted to perfluoroalkyl sulfonic acids. Sulfonic acids are intermediates of carboxylic acids. Sulfonyl fluorides also can be used as pesticides. Diperfluoroalkyl sulfoxones are applicable as dielectrics and solvents.

The preparation of sulfoxones with perfluorinated alkyl groups and of perfluoroalkylsulfonyl fluoride in a batch process in diglyme is described in GB-A 1189561. The process described there provides for the addition of sulfuryl fluoride (SO₂F₂) to specified fluorosubstituted alkenes. Alkali metal fluorides and quarternary ammonium fluorides are stated to be catalysts; the examples operate with CsF. While it is mentioned that the process described might be carried out at atmospheric or superatmospheric pressure, for potential reactants being gases or low boiling point liquids, use of superatmospheric pressure would be desirable.

WO 03/095422 discloses the preparation of a mixture of perfluoroethanesulfonyl fluoride and bis(perfluoroethyl)sulfone by reaction of perfluoroethylene with sulfuryl fluoride in DMF with potassium fluoride as catalyst.

EP 0 736 524 A discloses a process for the preparation of perfluoroisopropylsulfonyl fluoride by reaction of perfluoropropylene with sulfuryl fluoride in sulfolane with potassium fluoride as catalyst.

Objective of the present invention was to provide a technically simple process for the preparation of sulfonyl fluorides and sulfoxones by addition of sulfuryl fluoride to polyfluorosubstituted alkenes or perfluoroalkenes. This objective and other objectives are achieved by the process of the present invention.

The process of the present invention for the preparation of polyfluoroalkylsulfonyl fluorides or perfluoroalkylsulfonyl fluorides comprises a step wherein sulfuryl fluoride is continuously reacted with a
polyfluorosubstituted alkene or a perfluorinated alkene in the presence of a catalyst. The term “perfluorinated alkene” denotes alkenes in which all hydrogen atoms are substituted by fluorine. The term “polyfluorinated alkene” denotes alkenes in which at least 50 % of the hydrogen atoms are substituted by fluorine atoms. One or more of the other hydrogen atoms may be substituted by chlorine atoms, by an unsubstituted, partially fluorinated or perfluorinated alkyl group with 1 or 2 carbon atoms or by an unsubstituted alkoxy group with 1 or 2 carbon atoms or by an alkoxy group with fluorine substituents at the terminal carbon atom provided that, as mentioned above, at least 50 % of the hydrogen atoms of the alkene are substituted by fluorine atoms. “Unsubstituted” here means that these groups are substituted only by hydrogen. “Partially fluorinated” means that the alkyl group is substituted by at least one hydrogen atom, the remainder of substituents being fluorine atoms. Alkenes which consist of carbon and fluorine and optionally hydrogen are preferred. Perfluorinated alkenes are especially preferred starting compounds. Generally, alkenes with 2 to 12 carbon atoms can be applied in the process of the present invention. Alkenes that are very preferred are described in detail further below.

Especially preferably, the reaction is performed applying compounds with a boiling point (at 1 Bar) below the reaction temperature (thus, the starting compounds are gaseous or in a vapor state). More preferably, the reaction is performed with starting compounds with a boiling point at 1 bar (abs.) of equal to or lower than 15°C, especially equal to or lower than 0°C, and most preferred, equal to or lower than -10°C; hexafluoropropene for example, an especially preferred starting compound, has a boiling point of -29°C.

The invention will be explained in further detail for this preferred embodiment.

The surprising effect of continuously reacting sulfuryl fluoride and the fluorinated alkenes, especially hexafluoropropene, is the high yield. In example 1 of GB 1,189,561, hexafluoropropene is reacted with sulfuryl fluoride batch-wise with intermittent introduction of sulfuryl fluoride. This is a time-consuming process because several times, additional hexafluoropropene was introduced into the reactor after a pressure drop occurred. The fast, simply continuous process of the present invention yields comparable amounts of product or even more.

The reaction can be performed at elevated pressure. For example, the pressure can be equal to or less than 10 bars (abs). Preferably, the reaction is
performed at a pressure of equal to or lower than 5 bars, still more preferably equal to or lower than 2 bars (abs), especially preferably equal to or lower than 1.5 bars (abs.), still more preferably at a pressure equal to or lower than 1.3 bars (abs.). Preferably, the pressure is equal to or higher than 1 bar (abs.).

For example, the reaction can be performed without pressurization. The term “without pressurization” denotes a reaction wherein no external pressure, except for the ambient pressure (around 1 Bar), the delivery pressure of reactants and, if applied, the delivery pressure of inert gases like nitrogen is acting on the reaction mixture and scrubbers or washers acts on the reaction mixture. The range is often from 1 bar (abs) to 1.3 bars (abs.). Consequently, in a preferred embodiment, the reaction is, for example, not performed under autogenous pressure.

The residence time in any case is less than one hour.

Two reaction schemes are possible, as exemplified for perfluoro compounds:

1. \( \text{SO}_2\text{F}_2 + 1 \text{ perfluoroalkene} \rightarrow \text{perfluoroalkylsulfonyl fluoride} \) (I)
2. \( \text{SO}_2\text{F}_2 + 2 \text{ perfluoroalkene} \rightarrow (\text{diperfluoroalkyl})\text{sulfone} \) (II)

The same reaction scheme applies for polyfluoro compounds:

1. \( \text{polyfluoroalkene} + 1 \text{ SO}_2\text{F}_2 \rightarrow \text{polyfluoroalkylsulfonyl fluoride} \) (III)
2. \( 2 \text{ polyfluoroalkene} + 1 \text{ SO}_2\text{F}_2 \rightarrow (\text{dipolyfluoroalkyl})\text{sulfone} \) (IV)

In a first step, the 1:1 adduct is formed, namely perfluoroalkylsulfonyl fluoride or the respective poly fluoro compound. In a second step, if the molar ratio of alkene to sulfuryl fluoride is high enough so that unreacted alkene is still present in the reaction mixture, the 2:1 adduct is formed, namely a (diperfluoroalkyl)sulfone or a di(polyfluoroalkyl)sulfone. Commonly, the 2:1 adduct is formed if the molar ratio of alkene to sulfuryl fluoride is greater than 1. If it is desired to form a sulfone as end product by further reacting intermediately formed sulfonyl fluoride with alkene, the molar ratio of alkene to sulfuryl fluoride is preferably equal to or greater than 1.9:1, more preferably equal to or greater than 2:1. Thus, predominantly and even exclusively, the sulfones are formed as end product from the sulfonyl fluoride formed as intermediates.

Thus, one embodiment of the process of the present invention provides for the preparation of polyfluoroalkylsulfones or perfluoroalkylsulfones via the respective polyfluoroalkylsulfonyl fluoride or perfluoroalkylsulfonyl fluoride and comprises a step wherein sulfuryl fluoride is continuously reacted with a polyfluorosubstituted alkene or a perfluorinated alkene in a molar ratio of alkene
to sulfuryl fluoride greater than 1 in the presence of a catalyst. The reaction conditions for this embodiment preferably are preferably the same as described above for the preparation of the 1:1 adduct.

Accordingly, selecting the molar ratio of the alkene and sulfuryl fluoride in the desired manner provides for the preparation of a sulfonyl fluoride or a sulfone, respectively. If the molar ratio is in a higher range than 1 (ideal stoechiometric ratio 2:1), a sulfone is formed besides the sulfonyl fluoride or is even the only reaction product if the ratio of alkene to sulfuryl fluoride is high enough. If the molar ratio is in a lower range (ideal stoechiometric ratio 1:1), a sulfonyl fluoride is formed. Sometimes, mixtures of both products are obtained.

The preparation of perfluoroalkyl sulfonyl fluoride is preferred. Thus, the reaction is performed according to reaction schemes (I) and (II). For this preferred reaction, the molar ratio between $\text{SO}_2\text{F}_2$ and alkene preferably is equal to or higher than 0.8:1. The preferred molar ratio between $\text{SO}_2\text{F}_2$ and alkene for this reaction is equal to or lower than 1.2:1.

As mentioned above, perfluorinated alkenes consisting only of carbon and fluorine are preferred. In principle, many perfluorinated alkenes are suitable as starting compounds in the present reaction, for example, linear or branched perfluorinated alkenes with 2 to 12 carbon atoms. The suitability of a perfluoroalkene (or polyfluoroalkene, of course) can be checked by simple tests. In the context of the present invention, perfluorinated alkenes preferably correspond to formula (III), $\text{R}^1\text{-CF=CFR}^2$. $\text{R}^1$ and $\text{R}^2$ are the same or different and preferably denote perfluorinated C1-C4 alkyl or a fluorine atom. $\text{R}^1$ is preferably perfluormethyl or perfluoroethyl, and $\text{R}^2$ preferably denotes fluorine, perfluoromethyl or perfluoroethyl. Tetrafluoroethene and especially hexafluoropropene are highly suitable as starting compounds for the reaction with sulfuryl fluoride to produce perfluoroethyl sulfonyl fluoride and perfluoroisopropylsulfonyl fluoride.

The reaction is preferably performed in an aprotic organic solvent. The solvent must not react in an undesired manner with the starting material; this can be checked by simply mixing a desired solvent with the starting material. Preferably, the solvent has a boiling point higher than 60°C, more preferably higher than 70°C at ambient pressure (1 Bar). Examples of solvents applicable in the process of the present invention are dialkyl ethers, especially those of alkylene or polyalkylene glycols, dialkyl amides of carboxylic acids, preferably
dialkylamides of formic acid or carboxylic acids with a C1 to C4 alkyl group in
the acid group, especially dialkylamides of carboxylic acids with 1, 2 or
3 C atoms in the alkyl group in the acid group, and nitriles and dinitriles. For the
solvents described here, the terms “alkyl” and “alkylene” denotes groups with
1 to 4 carbon atoms; for example, the alkyl groups in the amide group of dialkyl
amides are groups with 1 to 4 C atoms. Dimethyl ethers of ethylene glycol,
diethylene glycol, triethylene glycol and tetraethylene glycols, dialkylamides of
formic acid, acetic acid, propionic acid and butyric acid, especially the respective
dimethylamides, and nitriles with a C1 to C5 alkyl group, adiponitrile or
benzonitrile are very suitable. Dimethylformamide is especially preferred.

The catalyst may be any catalyst known to catalyze the addition of sulfuryl
fluoride to fluorosubstituted alkenes. Catalysts comprising a halide ion,
especially a bromide or a fluoride ion, especially alkali metal fluorides and
quaternary ammonium fluorides with 4 alkyl groups with 1 to 4 carbon atoms,
especially those with linear alkyl groups, for example, tetramethylammonium
fluoride or tetraethylammonium fluoride, are preferred. KF and CsF are highly
preferred, especially KF.

The process according to the present invention preferably is performed at a
temperature of equal to or higher than 50°C, preferably equal to or higher
than 70°C. The upper limit is variable. Preferably, the reaction is performed at a
temperature of equal to or less than 170°C. A highly suitable temperature range
is 70 to 100°C.

Advantageously, the reactants are entered into the solvent in dispersed
form. For example, they can be passed through a frit into the solvent, especially
if they are in gaseous or vapor form. Alternatively or additionally, the reactor
may comprise means to improve the gas-liquid contact, especially means to
disperse gases or vapor in the liquid phase, for example, Pall rings or Raschig
rings or stirrers.

The most preferred embodiment of the present invention is directed to the
preparation of perfluoroisopropylsulfonyl fluoride wherein sulfuryl fluoride is
continuously reacted with hexafluoropropene in the presence of a catalyst,
preferably KF or CsF, in an aprotic solvent.

The process can be performed in a single reactor. If desired, reactants in
gaseous or vapor form can be passed through two, three, four or even more
consecutive reactors comprising solvent and catalyst. This may improve the
yield.
The isolation of the product can be performed in a known manner. Gaseous reaction products can be passed through cooled traps and condensed therein. If desired, they might be further purified by distillation, by a high-pressure distillation or deep-temperature distillation.

Reaction products with a higher boiling point can also be isolated continuously from the solvent, e.g. by distillation. For example, reaction mixture can be withdrawn from the reactor continuously, then, the desired product can be isolated, e.g. by distillation, and the remainder – mostly solvent – be returned to the reactor.

The process according to the present invention delivers a high yield per space and time. Preferably, the space-time yield is equal to or higher than 0.01 kg per liter of reactor volume and hour. More preferably, the space-time yield is equal to or higher than 0.05 kg per liter and hour, especially preferably, equal to or higher than 0.12 kg per liter and hour.

One advantage of the continuously performed process of the present invention is that yield is surprisingly good. Another advantage of certain preferred embodiments is that it can be performed in apparatus which need not be pressure-resistant.

The compounds prepared can be applied for any of the purposes they are known to be suitable for. Some fields of applications are given above. The most preferred compound, perfluoroisopropylsulfonyl fluoride, can be converted to salts of formula (IV) (CF₃)₂CFSO₃⁻ M⁺ wherein M⁺ denotes Li⁺, Na⁺, K⁺, Cs⁺, Rb⁺, R₄P⁺ or R₄N⁺ (here, R stands for C₁ to C₄ alkyl) as described in WO03/020691. These salts are suitable as electrolyte salts for Li ion batteries.

Of course, it is possible to react sulfonyl fluorides obtained according to the process of the present invention with further alkene to form sulfones according to known processes.

The following examples will explain the invention further without being intended to limit it.

Examples:

Example 1: Preparation of perfluoroisopropylsulfonyl fluoride
Apparatus: A reactor with an inner volume of 150 ml was connected via two inlet lines with two pressure bottles containing hexafluoropropene (HFP) and sulfonyl fluoride (SO₂F₂). The reactor was connected via an outlet line with a Liebig condenser which contained cooling water. The Liebig condenser was connected to a flask which was cooled in an ice bath. This flask was connected
with a trap cooled to -78°C. The reactor contained 115 ml (108 g) dimethylformamide (DMF) and 2.8 g KF as catalyst.

The temperature of the solvent was regulated to approximately 80°C during the introduction of the starting compounds. The starting compounds were passed continuously through the solvent. Gaseous reaction mixture leaving the reactor was passed through the cooled trap and condensed therein. Gaseous constituents not condensed in the trap left the trap into a scrubber.

1.1. HFP was introduced into the DMF solvent with a speed of 5.16 g/h (0.034 mol/h), SO$_2$F$_2$ with a speed of 3.2 g/h (0.031 mol/h). Product and unreacted starting material were condensed in the cooled trap. The product was isolated by low temperature distillation. The yield was 39.2 % of theory, based on the amount of HFP. The space time yield was calculated to be 0.0557 kg/L.h.

1.2. Example 1 was repeated, but this time, HFP was introduced with a speed of 13.14 g/h (0.088 mol/h), SO$_2$F$_2$ with a speed of 10.50 g/h (0.103 mol/h). This time, the yield was 38.8 %; space time yield was calculated to be 0.1576 kg/L.h.

Example 2 : Preparation of perfluoroisopropylsulfonyl fluoride in 2 consecutive reactors

Apparatus : A reactor with an inner volume of 150 ml was connected via two inlet lines with two pressure bottles containing hexafluoropropene (HFP) and sulfuryl fluoride (SO$_2$F$_2$). The reactor was connected via an outlet line with a Liebig condenser which contained cooling water. The Liebig condenser was connected to a flask which was cooled in an ice bath. This flask was connected to another reactor with an inner volume of 150 ml, which was connected via an outlet line with a Liebig condenser which contained cooling water. The Liebig condenser was connected to a flask which was cooled in an ice bath. In each reactor, 115 ml of DMF and 2.8 g of KF were contained. Both reactors were kept at 80°C. Gaseous constituents not condensed in the trap left the trap into a scrubber.

HFP was introduced into the mixture of solvent and catalyst in the first reactor in an amount of 35 g/h (0.23 mol/h), sulfuryl fluoride in an amount of 25 g/h (0.24 mol/h).

The yield was 56.2 % of the theory. The space time yield was 0.1587 kg/L.h.
Example 3: Preparation of perfluoroisopropylsulfonyl fluoride in 3 consecutive reactors

Example 2 is repeated, but this time, the reaction is performed in 3 consecutive reactors. The yield is still higher than in example 2.

The reactor in examples 1.1 and 1.2 and the reactors in examples 2 and 3 were operated at a pressure of about 1 to 1.2 bars (abs) because the exhaust from the cooled trap was an open line. This demonstrates that even with gaseous starting materials, no pressure needs to be applied, thus, no pressure apparatus is needed, nevertheless, high yields are obtained. But even when operating under pressure, the continuous process still is advantageous because of the surprisingly high yield.
CLAIMS

1. Process for the preparation of polyfluorosubstituted alkylsulfonyl fluorides and perfluoroalkylsulfonyl fluorides wherein sulfuryl fluoride is continuously reacted with polyfluorosubstituted alkenes or perfluorinated alkenes in the presence of a catalyst.

2. Process according to claim 1 wherein polyfluoro- or perfluoroalkylsulfonyl fluorides are prepared by reacting sulfuryl fluoride with a polyfluorosubstituted alkene or a perfluorinated alkene with a molar ratio of sulfuryl fluoride to perfluorinated alkene being equal to or less than 1.2:1.

3. Process according to claim 1 or 2 wherein an alkene of formula (I), 
\( R^1-\text{CF} \equiv \text{CFR}^2 \), is used as starting material, \( R^1 \) and \( R^2 \) being the same or different and denoting perfluorinated C1-C4-alkyl or a fluorine atom.

4. Process according to claim 3 wherein \( R^1 \) denotes perfluoromethyl or perfluoroethyl, and \( R^2 \) denotes fluorine, perfluoromethyl or perfluoroethyl.

5. Process according to claim 4 wherein \( R^1 \) denotes a fluorine atom and \( R^2 \) denotes a perfluoromethyl group and thus, the alkene is hexafluoropropene.

6. Process according to claim 1 wherein the reaction is performed in an aprotic solvent with a boiling point equal to or higher than 70°C.

7. Process according to claim 6 wherein the solvent is selected from the group of dialkyl ethers of alkylene glycols, dialkylamides of formic acid or of carboxylic acids with a C1 to C4 alkyl group, and nitriles with a C1 to C4 alkyl group, dinitriles with a C1 to C5 alkylene bridge or a phenyl group.

8. Process according to claim 1 wherein the reaction is performed at a temperature of equal to or higher than 70°C.

9. Process according to claim 1 wherein the reaction is performed at a temperature equal to or lower than 170°C.

10. Process according to claim 1 wherein the pressure is equal to or lower than 5 bars (abs.), preferably equal to or lower than 2 bars (abs.), especially preferably in the range of 1 to 1.3 Bars (absolute).
11. Process according to claim 1 wherein the reaction is performed in at least two consecutive reactors.

12. Process according to claim 1 wherein the molar ratio of polyfluoro- or perfluoroalkene to sulfuryl fluoride is greater than 1:1, preferably greater than 1.2:1, and thus, polyfluorosubstituted alkylsulfonyl fluorides and perfluoroalkylsulfonyl fluorides which are intermediately formed, are further reacted with unreacted polyfluoro- or perfluoroalkene to form (diperfluoroalkyl)sulfones or a di(polyfluoroalkyl)sulfones.

13. Process according to claim 12 wherein the molar ratio between the alkene and sulfuryl fluoride is equal to or greater than 2, and predominantly or exclusively, di(perfluoro)- or di(polyfluoro)sulfones are formed as end product.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C303/02 C07C309/80

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 practical, search terms used)

EPO-Internal, BEILSTEIN Data, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 03/095422 A (3M INNOVATIVE PROPERTIES) 20 November 2003 (2003-11-20) table 3, runs 29-46; claim 13</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search 8 October 2008

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