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A New Synthesis of Alkane and Polyfluoroalkanesulfonyl Chlorides

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ABSTRACT: *This study describes a new and advantageous procedure for the synthesis of alkanesulfonyl chlorides (**2**) by the reaction of alkyl thiocyanates (**1**) with sulfuryl chloride in a mixture of acetic acid and water. The alkanesulfonyl chlorides were obtained in good yields.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:355–361, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20559

INTRODUCTION

Alkanesulfonyl chlorides are known for their utility in imparting functionality into various compounds or as intermediates to modify various compounds including pharmaceuticals, agricultural chemicals, photographic chemicals, and the like, to increase their efficacy, to protect sensitive functional groups during certain processing steps, or to improve the recovery and purity during isolation procedures [1].

The use of alkanesulfonyl chlorides as the important precursors has been frequently encountered for the preparation of many diverse functional groups including sulfonates esters [2], sulfonamides [3], sulfonyl fluorides [4], sulfones [5], sulfinic acids [6], and others [7].

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A number of methods for the preparation of alkanesulfonyl chlorides have been described. Amongst these methods, the more important involve the aqueous chlorination of disulfides and thiols [8]. Different sulfur compounds have also been converted to alkanesulfonyl chlorides, e.g., thiols [8], sulfides [9], thiocyanates [10], isothiouronium salts [11], *S*,*S*-dialkyl dithiocarbonates [12], thiol esters [8], thiosulfonates [8], sulfinyl chlorides [13], and sulfinic acids [14]. However, the disadvantages of the most of these methods are the preparation of starting materials, or unsatisfactory reaction yields or the production of side products. Thus limiting convenient access to alkanesulfonyl chlorides.

In this paper, we describe a new preparation of alkanesulfonyl chloride starting from alkyl thiocyanates with sulfuryl chloride in acetic acid/ water media, which is a very effective and new pathway to synthesize these derivatives in good yields.

RESULTS AND DISCUSSION

A number of papers have been published on the synthesis of sulfonyl chlorides from thiocyanates using chlorine [10]. Chlorine gas in aqueous acetic acid has been used in the method. However, the use of chlorine gas is tedious and quite often causes a trouble. In the Table 1, we described a comparison of sulfuryl chloride and chlorine as chlorination agents of the alkyl thiocyanates [10].

TABLE 1 Comparison between SO_2Cl_2 and Cl_2 as Chlorination Agents of Alkyl Thiocyanates

	Chlorination Reactant	
	Sulfuryl Chloride	Chlorine
Yield	Very good (max 99%)	Good (max 79%)
Quantity of reactant	10 equiv	Large excess, not precise
Reaction time	Rapid (30 min—1 h)	Not precise
Manipulation	Easy	Tedious

The present method gives better reaction yields to the chlorine gas method with a much easier manipulation.

The alkanesulfonyl chlorides were prepared from alkyl bromide or chloride, in two steps, in good yields according to a method developed in our laboratory (Scheme 1).

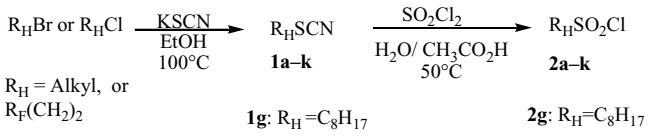
The reaction of alkyl bromide or chloride with potassium thiocyanate in absolute ethanol at 90°C gave the alkyl thiocyanates (**1**) in good yields.

We have now found that various alkyl thiocyanates and polyfluoroalkyl thiocyanates (**1**) reacted with sulfuryl chloride in the presence of a mixture of acetic acid and water at 50°C to lead to the corresponding sulfonyl chlorides (**2**) in excellent yields without any side products.

To find out optimum conditions, the reactions of **1g** with sulfuryl chloride in the presence of a mixture of water and acid were examined under various reaction conditions. In each case, we studied the conversion of **1g** in 160 min.

Influence of the Sulfuryl Chloride Molar Amount

When more than 5 equiv of sulfuryl chloride were used in a mixture of water and acetic acid at 50°C, **2g** was obtained in high yield. However, the chlorination reaction was achieved more rapidly with 10 equiv (1 equiv/min). With 2 equiv of sulfuryl chloride, we obtained 50% of formation of **2g** in 160 min. We used 10 equiv of sulfuryl chloride for the preparation of the others alkanesulfonyl chlorides. The results are summarized in Fig. 1.



SCHEME 1

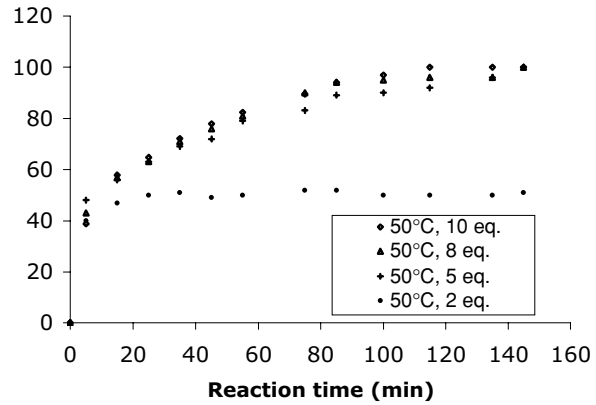


FIGURE 1 Effects of the equivalent amounts of sulfuryl chloride (1 equiv/min) on the conversion of **1g**. Reactions conditions: solvent: acetic acid, reaction temperature: 50°C. Note that the percentage of formation of **2g** was determined by ^{1}H NMR (acetone-d_6) by the relative integration of the functional C**H**$_2$ signal of **1g** compared with that of the functional C**H**$_2$ signal of **2g**.

Influence of the Reaction Temperature

We studied the effect of the variation of the temperature on rates of the chlorination. **1g** was chlorinated with 10 equiv of sulfuryl chloride (1 equiv/min) in a mixture of water and acetic acid.

Increases of the temperature resulted in increases of the formation of **2g** as could be seen in Fig. 2. At 25°C and 40°C, there were no more than, respectively, 83% and 94% of the chlorination of **1g** in 160 min.

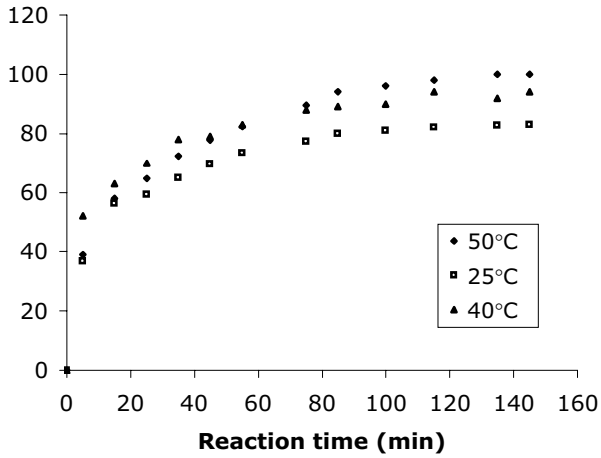


FIGURE 2 Effects of the reaction temperature on the conversion of **1g**. Reactions conditions: sulfuryl chloride = 10 equiv (1 equiv/min), solvent: acetic acid. Note that the percentage of formation of **2g** was determined by ^{1}H NMR (acetone-d_6) by the relative integration of the functional C**H**$_2$ signal of **1g** compared with that of the functional C**H**$_2$ signal of **2g**.

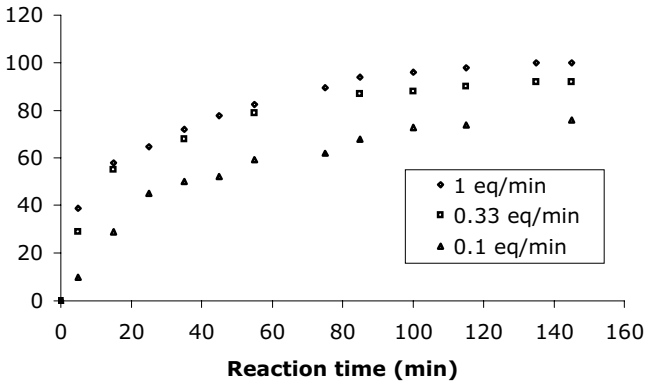


FIGURE 3 Effects of the addition rate of sulfuryl chloride on the conversion of **1g**. Reactions conditions: sulfuryl chloride = 10 equiv, solvent: acetic acid, reaction temperature: 50°C. Note that the percentage of formation of **2g** was determined by ^{1}H NMR (acetone-d_6) by the relative integration of the functional C**H**$_2$ signal of **1g** compared with that of the functional C**H**$_2$ signal of **2g**.

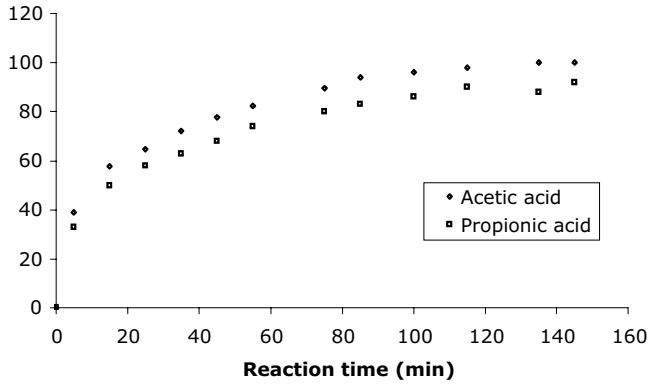


FIGURE 4 Effects of the solvent (propionic or acetic acid) on the conversion of **1g**. Reactions conditions: sulfuryl chloride = 10 equiv (1 equiv/min), reaction temperature: 50°C. The% of formation of **2g** was determined by ^{1}H NMR (acetone-d_6) by the relative integration of the functional C**H**$_2$ signal of **1g** compared with that of the functional C**H**$_2$ signal of **2g**.

Influence of the Sulfuryl Chloride Rate

We introduced 10 equiv of sulfuryl chloride that were added at different rates in a mixture of water and acetic acid at 50°C.

The chlorination reaction was achieved more rapidly with 10 equiv, which were added at the rate of 1 equiv/min. When the sulfuryl chloride was added at 0.33 equiv/min, the conversion of **1g** was not finished: There was 92% of formation of **2g** in 160 min.

In the same conditions, when the sulfuryl chloride was added more slowly, at the rate of 0.1 equiv/min, there was only 76% of formation of **2g**. The results are summarized in Fig. 3.

Influence of the Solvent

In addition the chlorination of **1g** is carried out in the presence of different solvents at 50°C along with 10 equiv of sulfuryl chloride (1 equiv/min).

When we used propionic acid instead of acetic acid, there was less chlorination of **1g** and there was 92% of chlorination with propionic acid (Fig. 4).

Influence of the Water

The reaction was performed in the absence or the presence of water. Without water, there was not the conversion of **1g**. The results are depicted in Fig. 5. The water is essential for the chlorination of thiocyanates that is an oxidation.

The best conditions for the chlorination of thiocyanates were the use of 10 equiv of sulfuryl chloride that were added at the rate of 1 equiv/min, in a mixture of acetic acid/ water at 50°C.

CONCLUSION

In summary, we have developed a new and efficient method for the synthesis of alkanesulfonyl chlorides and polyfluoroalkanesulfonyl chlorides starting from, respectively, alkyl thiocyanates and polyfluoroalkyl thiocyanates with sulfuryl chloride in a mixture of acetic acid and water. All alkanesulfonyl chlorides and polyfluoroalkanesulfonyl chlorides have been identified by comparison of their ^{1}H and ^{13}C NMR spectra with those authentic samples of analytical purity.

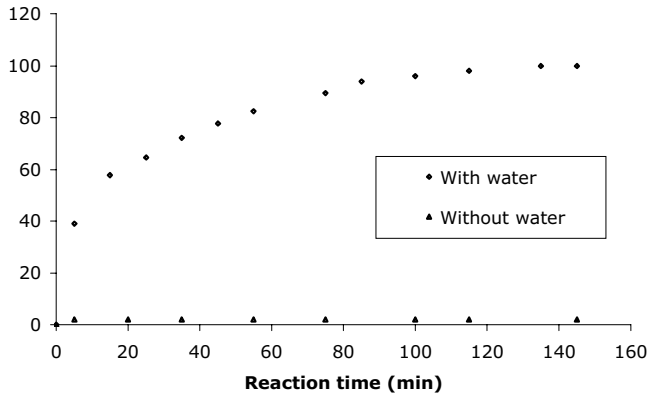


FIGURE 5 Effects of the water on the conversion of **1g**. Reaction conditions: sulfuryl chloride = 10 equiv (1 equiv/min), solvent: acetic acid, reaction temperature: 50°C. Note: The% of formation of **2g** was determined by ^{1}H NMR (acetone-d_6) by the relative integration of the functional C**H**$_2$ signal of **1g** compared with that of the functional C**H**$_2$ signal of **2g**.

EXPERIMENTAL

General

Different alkyl bromides (R_HBr) or alkyl iodides (R_HI) were purchased from Aldrich (Saint Quentin Fallavier, France). Different polyfluoroalkyl iodides ($R_F(CH_2)_2I$) were purchased from Elf Atochem (Pierre Bénite, France). Solvents were distilled from the appropriate drying agents immediately prior to use.

^1H, ^{19}F, and ^{13}C NMR spectra were recorded at 300.13, 282.37, and 75.46 MHz, respectively, with a Bruker Avance 300 spectrometer; therefore, chemical shifts were given in ppm relative to Me_4Si, CCl_3F, respectively, as internal standards. Coupling constants are given in hertz.

Melting points were recorded at atmospheric pressure unless otherwise stated on a Stuart scientific SMP3 apparatus and remained without any correction.

Identifications of all the products, which are already known, were performed according to the literature by comparison with authentic samples.

Note that for each kinetic of formation of **2g** we used 5 g of **1g**.

*Synthesis of Alkyl Thiocyanates (**1a–1j**)*

General Procedure for the Synthesis of Alkyl Thiocyanates. To a solution of R_HBr or $R_F(CH_2)_2I$ (1 equiv) dissolved in absolute ethanol, potassium thiocyanate (1.5 equiv) was added. The reaction mixture was refluxed for 5 h. After cooling, all volatile parts of the mixture were removed in vacuo. The residue was dissolved in EtOAc and washed successively with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to yield the corresponding alkyl thiocyanates, which were used in the next step without any purification.

*Synthesis of Propyl Thiocyanate (**1a**).* Five grams (29.41 mmol) of propyl iodide in 40 mL of absolute ethanol was refluxed with 4.28 g (44.12 mmol) of potassium thiocyanate, and 2 g of **1a** was obtained (67%).

^1H NMR (300.13 MHz, d_6-acetone): δ 0.90 (t, $J = 7.3$ Hz, 3H, C**H**$_3$), 1.72 (m, 2H, $CH_3C\mathbf{H}_2$), 3.02 (t, $J = 7$ Hz, 2H, C**H**$_2$SCN); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 17.93 (**C**H_3CH_2), 29.38 ($CH_3\mathbf{C}H_2$), 41.54 (**C**H_2SCN), 118.03 (S**C**N).

*Synthesis of Butyl Thiocyanate (**1b**).* Five grams (36.49 mmol) of butyl iodide in 40 mL of absolute ethanol was refluxed with 5.31 g (54.73 mmol) of potassium thiocyanate, and 4.15 g of **1b** was obtained (99%).

^1H NMR (300.13 MHz, d_6-acetone): δ 0.85 (t, $J = 7.4$ Hz, 3H, C**H**$_3$), 1.40 (m, 2H, $CH_3C\mathbf{H}_2$), 1.69 (m, 2H, $CH_3CH_2C\mathbf{H}_2$), 2.96 (t, $J = 7.2$ Hz, 2H, C**H**$_2$SCN); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 13.68 (**C**H_3), 21.70 ($CH_3\mathbf{C}H_2$), 32.78 (**C**H_2CH_2SCN), 34.15 (**C**H_2SCN), 112.84 (S**C**N).

*Synthesis of 2-Methylpropyl Thiocyanate (**1c**).* Five grams (36.49 mmol) of 2-methylpropyl bromide in 40 mL of absolute ethanol was refluxed with 5.31 g (54.73 mmol) of potassium thiocyanate, and 4.15 g of **1c** was obtained (99%).

^1H NMR (300.13 MHz, d_6-acetone): δ 0.94 (d, $J = 6.7$ Hz, 6H, **2**C**H**$_3$), 1.95 (m, 1H, C**H**), 2.90 (d, $J = 6.81$ Hz, 2H, C**H**$_2$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 21.23 (**2C**H_3), 30.09 (**C**H), 42.75 (**C**H_2SCN), 113.14 (S**C**N).

*Synthesis of 3-Methylbutyl Thiocyanate (**1d**).* Five grams (33.10 mmol) of 3-methylbutyl bromide in 40 mL of absolute ethanol was refluxed with 4.81 g (49.66 mmol) of potassium thiocyanate, and 3.12 g of **1d** was obtained (73%).

^1H NMR (300.13 MHz, d_6-acetone): δ 0.81 (d, $J = 6.4$ Hz, 6H, **2**C**H**$_3$), 1.63 (m, 3H, C**H**, C**H**$_2$), 2.99 (t, $J = 7.5$ Hz, 2H, C**H**$_2$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 22.40 (**C**H_3), 27.61 (**C**H), 32.64 (**C**H_2SCN), 39.69 (**C**H_2CH_2SCN), 112.81 (S**C**N).

*Synthesis of Hexyl Thiocyanate (**1e**).* Twenty grams (122 mmol) of hexyl bromide in 100 mL of absolute ethanol was refluxed with 17.74 g (183 mmol) of potassium thiocyanate, and 16.1 g of **1e** was obtained (92%).

^1H NMR (300.13 MHz, d_6-acetone): δ 0.81 (t, 3H, C**H**$_3$), 1.32 (m, 4H, $CH_3(C\mathbf{H}_2)_2$), 1.55 (m, 2H, C**H**$_2(CH_2)_2$SCN), 1.69 (m, 2H, C**H**$_2CH_2$SCN), 2.95 (t, $J = 7.25$, 2H, C**H**$_2$SCN); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 14.35 (**C**H_3), 23.18, 31.86 (**2C**H_2), 30.76 (**C**$H_2(CH_2)_2$SCN), 28.27 (**C**H_2CH_2SCN), 34.50 (C**H**$_2$SCN), 117.98 (S**C**N).

*Synthesis of Octyl Thiocyanate (**1f**).* Twenty-three grams (120 mmol) of octyl bromide in 100 mL of absolute ethanol was refluxed with 17.34 g (180 mmol) of potassium thiocyanate, and 18 g of **1g** was obtained (88%).

^1H NMR (300.13 MHz, d_6-acetone): δ 0.91 (t, $J = 6.9$ Hz, 3H, C**H**$_3$), 1.40 (m, 10H, $CH_3(C\mathbf{H}_2)_5$), 1.86 (m, 2H, C**H**$_2CH_2$SCN) 3.10 (t, $J = 7.2$ Hz, 2H, C**H**$_2$SCN); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 14.46 (**C**H_3), 23.35, 28.60, 29.65, 30.80, 32.54 (**5C**H_2), 29.88 (**C**H_2CH_2SCN), 34.49 (**C**H_2SCN), 112.77 (S**C**N).

*Synthesis of Decyl Thiocyanate (***1g***).* Five grams (22.61 mmol) of decyl bromide in 40 mL of absolute ethanol was refluxed with 3.29 g (33.91 mmol) of potassium thiocyanate, and 4.46 g of **1g** was obtained (99%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 0.78 (t, $J = 6.5$ Hz, 3H, C**H**$_3$), 1.25 (m, 14H, CH$_3$(C**H**$_2$)$_7$), 1.71 (m, 2H, C**H**$_2$CH$_2$SCN), 3.02 (t, $J = 7.25$ Hz, 2H, C**H**$_2$SCN); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 14.44 (**C**H$_3$), 23.38, 28.58, 29.67, 30.02, 30.07, 30.28, 32.66 (7**C**H$_2$), 30.79 (**C**H$_2$CH$_2$SCN), 34.46 (**C**H$_2$SCN), 111.06 (S**C**N).

*Synthesis of 3,3,4,4,5,5,6,6,6-Nonafluorohexyl Thiocyanate (***1h***).* Forty grams (107 mmol) of C$_4$F$_9$(CH$_2$)$_2$I in 300 mL of absolute ethanol was refluxed with 16 g (160 mmol) of potassium thiocyanate, and 32 g of **1h** was obtained (98%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 2.85 (m, 2H, C$_4$F$_9$C**H**$_2$), 3.48 (m, 2H, C$_4$F$_9$CH$_2$C**H**$_2$); ^{19}F NMR (282.37 MHz, d_6-acetone): δ −126.84 (m, 2F, CF$_3$C**F**$_2$), −125.02 (m, 2F, CF$_3$CF$_2$C**F**$_2$), −114.74 (m, 2F, CF$_3$(CF$_2$)$_2$C**F**$_2$), −82.2 (m, 3F, **C**F$_3$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 25.61 (**C**H$_2$SCN), 32.37 (CF$_2$**C**H$_2$), 111.83 (S**C**N), 111–124 (**C**$_4$F$_9$).

*Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl Thiocyanate (***1i***).* Sixty grams (127 mmol) of C$_6$F$_{13}$(CH$_2$)$_2$I in 450 mL of absolute ethanol was refluxed with 18.4 g (190 mmol) of potassium thiocyanate, and 46.20 g of **1i** was obtained (90%).

mp = 40–41°C. ^{1}H NMR (300.13 MHz, d_6-acetone): δ 2.85 (m, 2H, C$_6$F$_{13}$C**H**$_2$), 3.48 (m, 2H, C$_6$F$_{13}$CH$_2$C**H**$_2$); ^{19}F NMR (282.37 MHz, d_6-acetone): δ −126.77 (m, 2F, CF$_3$C**F**$_2$), −123.93 (m, 2F, CF$_3$CF$_2$C**F**$_2$), −123.44 (m, 2F, CF$_3$(CF$_2$)$_2$C**F**$_2$), −122.45 (m, 2F, CF$_3$(CF$_2$)$_3$C**F**$_2$), −114.35 (m, 2F, CF$_3$(CF$_2$)$_4$C**F**$_2$), −81.75 (m, 3F, C**F**$_3$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 26.13 (**C**H$_2$SCN), 32.78 (CF$_2$**C**H$_2$), 112.42 (S**C**N), 111–124 (**C**$_6$F$_{13}$).

*Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl Thiocyanate (***1j***).* Sixty grams (105 mmol) of C$_8$F$_{17}$(CH$_2$)$_2$I in 450 mL of absolute ethanol was refluxed with 15.21 g (157 mmol) of potassium thiocyanate, and 52.27 g of **1j** was obtained (99%).

mp = 67–68°C. ^{1}H NMR (300.13 MHz, d_6-acetone): δ 2.85 (m, 2H, C$_8$F$_{17}$C**H**$_2$), 3.48 (m, 2H, C$_6$F$_{17}$CH$_2$C**H**$_2$), ^{19}F NMR (282.37 MHz, d_6-acetone): δ −126.70 (s, 2F, CF$_3$C**F**$_2$), −123.91 (m, 2F, CF$_3$CF$_2$C**F**$_2$), −123.2 (m, 2F, CF$_3$(CF$_2$)$_2$C**F**$_2$), −122.32 (m, 6F, CF$_3$(CF$_2$)$_3$(C**F**$_2$)$_3$), −114.27 (m, 2F, CF$_3$(CF$_2$)$_6$C**F**$_2$), −81.60 (m, 3F, C**F**$_3$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 25.70 (**C**H$_2$SCN), 32.42 (CF$_2$**C**H$_2$), 111.98 (S**C**N), 111–124 (**C**$_8$F$_{17}$).

*Synthesis of Alkanesulfonyl Chloride (***2a–2j***)*

General Procedure for the Synthesis of Alkanesulfonyl Chloride. Alkyl thiocyanates (1 equiv) dissolved in a mixture of acetic acid (5 equiv) and water (1.5 equiv) were stirred for 30 min at 50°C. Sulfuryl chloride (SO$_2$Cl$_2$, 10 equiv) was added dropwise to the reaction mixture at 50°C. This reaction was accompanied by a strong emission of gases (SO$_2$ and Cl$_2$), which were trapped with an aqueous solution of NaOH (1 M). The excess of SO$_2$Cl$_2$, present in the media, was hydrolyzed by dropwise addition of water. The crude product was extracted three times with EtOAc. The combined organic extracts were washed three times with water, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated giving a crude material alkanesulfonyl chloride, which could be used without further purification.

*Synthesis of Propanesulfonyl Chloride (***2a***).* 1.22 g (12.08 mmol) of **1a** dissolved in a mixture of 3.5 mL (60.4 mmol) of acetic acid and 0.32 mL (18.1 mmol) of water was stirred 30 min at 50°C with 9.8 mL (120.8 mmol) of SO$_2$Cl$_2$. The excess of SO$_2$Cl$_2$ was hydrolyzed by the addition of water (10 mL). The crude product was extracted with 3 × 5 mL of EtOAc, and 1.70 g of **2a** [15] was obtained (99%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 1.05 (t, $J = 7.4$ HZ; 3H, C**H**$_3$), 1.95 (m, 2H, CH$_3$C**H**$_2$), 3.88 (m, 2H, C**H**$_2$SO$_2$Cl); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 12.27 (**C**H$_3$CH$_2$), 19.11 (CH$_3$**C**H$_2$), 67.37 (**C**H$_2$SO$_2$Cl).

*Synthesis of Butanesulfonyl Chloride (***2b***).* Two grams (17.39 mmol) of **1b** dissolved in a mixture of 5 mL (86.96 mmol) of acetic acid and 0.47 mL (26.09 mmol) of water was stirred 30 min at 50°C with 14.1 mL (173.9 mmol) of SO$_2$Cl$_2$. The excess of SO$_2$Cl$_2$ was hydrolyzed by the addition of water (10 mL). The crude product was extracted with 3 × 5 mL of EtOAc, and 2.64 g of **2b** [16] was obtained (97%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 0.85 (m, 3H, C**H**$_3$), 1.49 (m, 2H, CH$_3$C**H**$_2$), 1.90 (m, 2H, CH$_3$CH$_2$C**H**$_2$), 3.90 (t, $J = 7$ Hz, 2H, C**H**$_2$SO$_2$Cl); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 13.74 (**C**H$_3$), 21.37 (CH$_3$**C**H$_2$), 27.20 (**C**H$_2$CH$_2$SO$_2$Cl), 65.70 (**C**H$_2$SO$_2$Cl).

*Synthesis of 2-Methylpropanesulfonyl Chloride (***2c***).* One gram (8.69 mmol) of **1c** dissolved in a mixture of 2.5 mL (43.45 mmol) of acetic acid and 0.23 mL (13 mmol) of water was stirred 30 min at 50°C with 7 mL (86.95 mmol) of SO$_2$Cl$_2$. The excess

of SO_2Cl_2 was hydrolyzed by the addition of water (10 mL). The crude product was extracted with 3 × 5 mL of EtOAc, and 1.35 g of **2c** [17] was obtained (95%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 1.05 (d, $J = 6.77$ Hz, 6H, **2**C**H**$_3$), 2.32 (m, 1H, C**H**), 3.85 (d, $J = 6.47$ Hz, 2H, **C**H$_2$SO$_2$Cl); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 19.55 (2**C**H$_3$), 24.62 (**C**H), 71.28 (**C**H$_2$SO$_2$Cl).

*Synthesis of 3-Methylbutanesulfonyl Chloride (**2d**).* Two grams (15.51 mmol) of **1d** dissolved in a mixture of 4.4 mL (77.55 mmol) of acetic acid and 0.42 mL (23.3 mmol) of water was stirred 30 min at 50°C with 12.6 mL (155.1 mmol) of SO_2Cl_2. The excess of SO_2Cl_2 was hydrolyzed by the addition of water (10 mL). The crude product was extracted with 3 × 5 mL of EtOAc, and 2.17 g of **2d** was obtained (82%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 0.90 (d, $J =$ 6.5 Hz, 6H, **2**C**H**$_3$), 1.80 (m, 3H, C**H**, C**H**$_2$), 3.90 (m, 2H, C**H**$_2$SO$_2$Cl); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 22.35 (2**C**H$_3$), 27.67, 33.61 (**C**H and **C**H$_2$CH$_2$SO$_2$Cl), 64.55 (**C**H$_2$SO$_2$Cl).

*Synthesis of Hexanesulfonyl Chloride (**2e**).* Two grams (13.98 mmol) of **1e** dissolved in a mixture of 4 mL (69.9 mmol) of acetic acid and 0.38 mL of water (20.98 mmol) was stirred 30 min at 50°C with 11.3 mL (139.86 mmol) of SO_2Cl_2. The excess of SO_2Cl_2 was hydrolyzed by the addition of water (10 mL). The crude product was extracted with 3 × 5 mL of EtOAc, and 2.4 g of **2e** [16] was obtained (93%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 0.90 (m, 3H, C**H**$_3$), 1.35 (m, 4H, CH$_3$(C**H**$_2$)$_2$), 1.57 (m, 2H, C**H**$_2$(CH$_2$)$_2$SO$_2$Cl), 2.00 (m, 2H, C**H**$_2$CH$_2$SO$_2$Cl), 4.00 (m, 2H, C**H**$_2$SO$_2$Cl); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 14.23 (**C**H$_3$), 22.97, 27.72, 31.78 (**3C**H$_2$), 24.87 (**C**H$_2$CH$_2$SO$_2$Cl), 65.92 (**C**H$_2$SO$_2$Cl).

*Synthesis of Octanesulfonyl Chloride (**2f**).* Two grams (11.69 mmol) of **1f** dissolved in a mixture of 3.3 mL (58.45 mmol) of acetic acid and 0.32 mL (17.54 mmol) of water was stirred 30 min at 50°C with 9.48 mL (116.90 mmol) of SO_2Cl_2. The excess of SO_2Cl_2 was hydrolyzed by the addition of water (10 mL). The crude product was extracted with 3 × 5 mL of EtOAc and 2.15 g of **2f** [16] was obtained (86%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 0.91 (m, 3H, C**H**$_3$), 1.52 (m, 10H, CH$_3$(C**H**$_2$)$_5$), 2.04 (m, 2H, C**H**$_2$CH$_2$SO$_2$Cl), 3.80 (m, 2H, C**H**$_2$SO$_2$Cl); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 14.5 (**C**H$_3$), 23.40, 25.4, 25.60, 27.80, 29.60, 32.60 (6**C**H$_2$), 65.80 (**C**H$_2$SO$_2$Cl).

*Synthesis of Decanesulfonyl Chloride (**2g**).* Four grams (20.10 mmol) of **1g** dissolved in a mixture of 5.75 mL (100.5 mmol) of acetic acid and 0.54 mL of water (30.15 mmol) was stirred 30 min at 50°C with 16.29 mL (201 mmol) of SO_2Cl_2. The excess of SO_2Cl_2 was hydrolyzed by the addition of 10 mL of water. The crude product was extracted with 3 × 5 mL of EtOAc, and 4.6 g of **2g** was obtained (95%).

^{1}H NMR (300.13 MHz, d_6-acetone): δ 0.78 (d, $J = 6.5$ Hz, 3H, C**H**$_3$), 1.37 (m, 14H, CH$_3$(C**H**$_2$)$_7$), 1.99 (m, 2H, C**H**$_2$CH$_2$SO$_2$Cl), 3.99 (t, $J = 7.8$ Hz, 2H, C**H**$_2$SO$_2$Cl); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 14.39 (**C**H$_3$), 22.63, 24.27, 27.55, 28.87, 29.15, 29.19, 29.38, 31.81 (8**C**H$_2$), 65.78 (**C**H$_2$SO$_2$Cl).

*Synthesis of 3,3,4,4,5,5,6,6,6-nonafluorohexanesulfonyl Chloride (**2h**).* Twenty-nine grams (95 mmol) of **1h** dissolved in a mixture of 27 mL (475 mmol) of acetic acid and 2.6 mL (142.5 mmol) of water was stirred 1.5 h at 50°C with 77 mL (950 mmol) of SO_2Cl_2. The excess of SO_2Cl_2 was hydrolyzed by the addition of water (60 mL). The crude product was extracted with 3 × 20 mL of EtOAc, and 29.64 g of **2h** was obtained (90%). The compound **2h** synthesized previously was compared by ^{1}H NMR spectroscopy with pure sample furnished by Elf-Atochem.

^{1}H NMR (300.13 MHz, d_6-acetone): δ 3.05 (m, 2H, C$_4$F$_9$C**H**$_2$), 4.45 (m, 2H, C$_4$F$_9$CH$_2$C**H**$_2$); ^{19}F NMR (282.37 MHz, d_6-acetone): δ −126.70 (m, 2F, CF$_3$C**F**$_2$), −124.65 (m, 2F, CF$_3$CF$_2$C**F**$_2$), −113.80 (m, 2F, CF$_3$(CF$_2$)$_2$C**F**$_2$), −82.10 (m, 3F, **C**F$_3$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 27.52 (CF$_2$**C**H$_2$), 57.05 (**C**H$_2$SO$_2$Cl), 111–124 (**C**$_4$F$_9$).

*Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctanesulfonyl Chloride (**2i**).* Thirty grams (74 mmol) of **1i** dissolved in a mixture of 21 mL (370 mmol) of acetic acid and 2 mL (111 mmol) of was stirred 1.5 h at 50°C with 60 mL of SO_2Cl_2 (740 mmol). The excess of $SO_2Cl_2$was hydrolyzed by the addition of water (60 mL). The crude product was extracted with 3 × 25 mL of EtOAc, and 32.98 g of **2i** was obtained (100%). The compound **2i** synthesized previously was compared by ^{1}H NMR spectroscopy with pure sample furnished by Elf-Atochem.

mp = 28°C. ^{1}H NMR (300.13 MHz, d_6-acetone): δ 3.10 (m, 2H, C$_6$F$_{13}$C**H**$_2$), 4.48 (m, 2H, CH$_2$C**H**$_2$), ^{19}F NMR (282.37 MHz, d_6-acetone): δ −127.04 (m, 2F, CF$_3$C**F**$_2$), −123.87 (m, 4F, CF$_3$CF$_2$(C**F**$_2$)$_2$), −122.62 (m, 2F, CF$_3$(CF$_2$)$_3$C**F**$_2$), −113.70 (m, 2F, CF$_3$(CF$_2$)$_4$C**F**$_2$), −82.12 (m, 3F, C**F**$_3$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 27.64 (CF$_2$**C**H$_2$), 57.11 (**C**H$_2$SO$_2$Cl), 111–124 (**C**$_6$F$_{13}$).

*Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorooctanesulfonyl Chloride (**2j**).* Thirty-four grams (67 mmol) of **1j** dissolved in a mixture of 19 mL (335 mmol) of acetic acid and 2 mL (100.5 mmol) of water was stirred 1.5 h at 50°C with 55 mL of SO_2Cl_2 (670 mmol). The excess of SO_2Cl_2 was hydrolyzed by the addition of water (90 mL). The crude product was extracted with 3 × 30 mL of EtOAc, and 37.33 g of **2j** was obtained (100%). The compound **2j** synthesized previously was compared by ^{1}H NMR spectroscopy with pure sample furnished by Elf-Atochem.

mp = 65°C. ^{1}H NMR (300.13 MHz, d_6-acetone): δ 3.05 (m, 2H, $C_8F_{17}C\mathbf{H}_2$), 4.40 (m, 2H, $CH_2C\mathbf{H}_2$); ^{19}F NMR (282.37 MHz, d_6-acetone): δ −126.81 (s, 2F, $CF_3C\mathbf{F}_2$), −123.62 (m, 2F, $CF_3CF_2C\mathbf{F}_2$), −123.31 (m, 2F, $CF_3(CF_2)_2C\mathbf{F}_2$), −122.33 (m, 6F, $CF_3(CF_2)_3(C\mathbf{F}_2)_3$), −113.36 (m, 2F, $CF_3(CF_2)_6C\mathbf{F}_2$), −81.81 (m, 3F, $C\mathbf{F}_3$); ^{13}C NMR (75.46 MHz, d_6-acetone): δ 27.33 ($CF_2\mathbf{C}H_2$), 57.11 ($\mathbf{C}H_2SO_2Cl$), 111–122 ($\mathbf{C}_8F_{17}$).

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