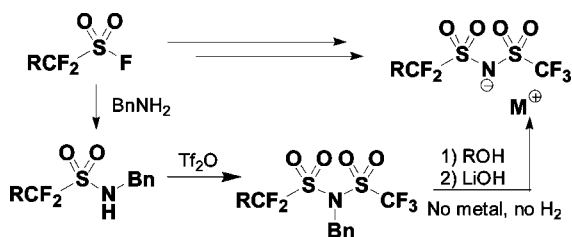# Efficient Preparation of New Fluorinated Lithium and Ammonium Sulfonimides

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ICBMS, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Equipe SERCOF, 43 boulevard du 11 novembre 1918, Villeurbanne, F-69622, France, CNRS, UMR5246, Villeurbanne, F-69622, France, Université de Lyon, Lyon, F-69622, France, Université Lyon 1, Lyon, F-69622, France, INSA-Lyon, Villeurbanne, F-69622, France, and CPE Lyon, Villeurbanne, F-69616, France

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An efficient preparation of new fluorinated lithium and ammonium sulfonimides, from the corresponding sulfonyl fluorides, is reported. These sulfonyl fluorides are reacted with benzylamine, then triflated. Due to the high leaving ability of fluorinated sulfonimides, the formed *N*-benzylsulfonimides are simply debenzylated with an alcohol. Finally, the intermediate oxonium sulfonimides are neutralized, in situ, by various bases. The obtained sulfonimides are potential electrolytes for lithium batteries or fuel cells.

Introduction

Nowadays, electricity production and storage is a major challenge for reducing global warming. Lithium batteries are already popular for small electronic devices but are not yet adapted for future applications. To circumvent the current drawbacks, new electrodes and new electrolytes have to be designed.[1] Considering electrolytes, $LiPF_6$ is currently used, but its development in batteries operating at 80−90 °C is hindered by a moderate thermal and hydrolytic stability and by the toxicity of its decomposition products. As for $(CF_3SO_2)_2NLi$ (LiTFSI), its high conductivity and its high thermal and electrochemical stabilities make it a promising salt. However,

at the high oxidation potentials of lithium ion batteries, it corrodes the aluminum electrode collector connected to the positive electrode.[1] So, a growing interest is being paid to new and efficient sulfonimide salts. It can be noticed that sulfonimides have also received attention in recent years as ionic liquids,[2] electrolytes for fuel cells,[3] or acid catalysts.[4] For all these applications, it must be emphasized that fluorinated anions are inescapable because of their very low basicity, nucleophilicity, and oxidability.
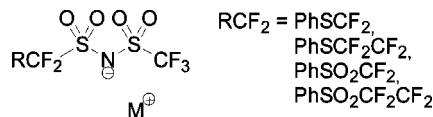

FIGURE 1. Structure of the desired sulfonimide salts.

As we recently developed new sulfonyl fluorides,[5] we used them to prepare a new class of sulfonimides (Figure 1) which could provide electrolytes with better properties than LiTFSI.

Since the discovery of LiTFSI,[6a] a large number of perfluoroalkanesulfonimide salts[7] have been prepared, but only few of them contain an aromatic ring.[8,9] The sulfonimide salts we plan to describe here are complementary to them, as they are constituted by an aromatic part separated by a linker from a fluorinated moiety. This linker can be a sulfide function, that brings some flexibility to the molecules, or a sulfone, which enhances the electron withdrawing properties and the polarity of the anion. The aromatic group could also allow the introduction of various substituents or functions enabling the preparation of ionomers.

Two main methods have been described to prepare fluoroalkanesulfonimides: the reaction of sulfonyl fluorides with trifluoromethanesulfonamide in the presence of a base[9,10] or with the sodium salt of *N*-(trimethylsilyl)trifluoromethylsulfonamide.[6,11]

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SCHEME 1. First Attempts To Synthesize 2a
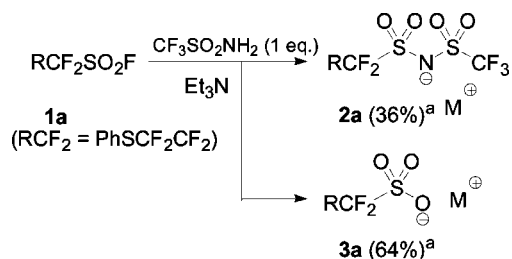
a Proportions determined by ^{19}F NMR.

SCHEME 2. Proposed Retrosynthesis To Prepare Lithium Sulfonimides
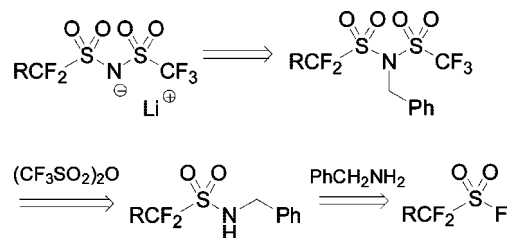
Other methods can be mentioned, such as the reaction of sulfonyl fluorides with ammonia,[12] silazanes,[13] or trifluoroacetamide.[14] Unfortunately, when applied to our substrates, some of these methods were not as efficient as expected.

Indeed, when reacting trifluoromethanesulfonamide with sulfonyl fluoride **1a**, in the presence of triethylamine, the corresponding ammonium sulfonimide **2a** was formed but along a major amount of the corresponding sulfonate **3a** resulting from a competitive hydrolysis of **1a**, whatever the precautions taken (Scheme 1).

This coupling reaction was found to be very moisture sensitive, and as CF$_3$SO$_2$NH$_2$ or CF$_3$SO$_2$N(Na)TMS are very poor nucleophiles, they could not kinetically compete with moisture. Thus, we report here an improved synthesis to circumvent this difficulty. A new strategy was considered: first, creation of the sulfur–nitrogen bond, then introduction of the SO$_2$CF$_3$ moiety. Benzylamine was chosen as the key nucleophile to build the S–N bond since benzylamine is a good nucleophile and the *N*-benzyl bond is known to be cleaved under a variety of procedures (Scheme 2).

Results and Discussion

For the first step, benzylamine was used in excess and *N*-benzylsulfonamides **4a**−**d** were obtained in good to excellent yields (Table 1) since hydrolysis was almost completely suppressed. Compounds **4a**−**d** were easily purified by chromatography.

TABLE 1. Synthesis of *N*-Benzylsulfonamides

entry	RCF$_2$	RCF$_2$SO$_2$F	product	yield (%)
1	C$_6$H$_5$SCF$_2$CF$_2$	**1a**	**4a**	77
2	C$_6$H$_5$SCF$_2$	**1b**	**4b**	90
3	C$_6$H$_5$SO$_2$CF$_2$CF$_2$	**1c**	**4c**	83
4	C$_6$H$_5$SO$_2$CF$_2$	**1d**	**4d**	78^a

a Reaction performed between −20 °C and rt.

SCHEME 3. Side Formation of 5
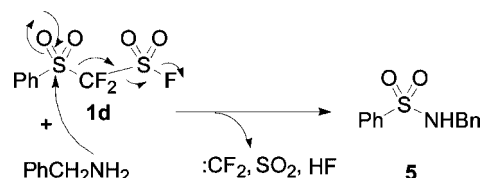
TABLE 2. Synthesis of *N*-Benzylsulfonimides

entry	RCF$_2$	product	yield^a (%)
1	C$_6$H$_5$SCF$_2$CF$_2$	**6a**	92
2	C$_6$H$_5$SCF$_2$	**6b**	89^b
3	C$_6$H$_5$SO$_2$CF$_2$CF$_2$	**6c**	81
4	C$_6$H$_5$SO$_2$CF$_2$	**6d**	81

a Reaction performed with 1 equiv of DIEA and 1.5 equiv of triflic anhydride unless otherwise noted. *b* With 1.1 equiv of DIEA, aqueous workup before extraction of **6b** from the residue.

It can be noticed that when **1d** was reacted with benzylamine at 50 °C, a side reaction occurred that led to the contamination of **4d** by *N*-benzylbenzenesulfonamide **5** (ratios **4d/5**: 1/1.7). This side reaction could result from the attack of benzylamine on the very electrophilic sulfonyl group of **1d**, followed by expulsion of difluorocarbene, SO$_2$, and a fluoride (Scheme 3). Such a reaction exhibits some similarity with the generation of a trifluoromethyl anion from *t*-BuOK and (trifluoromethanesulfonyl)benzene.[15] Unfortunately, we were not able to obtain any evidence of difluorocarbene formation. In contrast, this side reaction was never observed with sulfonyl fluoride **1c**.

Nevertheless, *N*-benzylsulfonamide **4d** was obtained pure in a 78% yield (Table 1, entry 4) when the reaction was performed at lower temperatures (−20 °C to rt).

In a second step, *N*-benzylsulfonimides **6a**−**d** were obtained in excellent yields (Table 2) by subsequent reaction with triflic anhydride in the presence of diisopropylethylamine (DIEA). The formed ammonium triflates were easily separated from **6a**−**d**, which were extracted in pentane.

The deprotection of **6a**−**d** was then examined. Usually, *N*-benzyl bonds are cleaved by palladium-catalyzed hydrogenolysis. Surprisingly, we observed that deprotection occurred after addition of **6a**−**d** to ethanol, prior introduction of hydrogen

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TABLE 3. Synthesis of Lithium Sulfonimides

	1) EtOH, r.t
6a-d	2) Base (1 eq.), r.t. → 7a-d (M⁺ = Li⁺), 2a-b (M⁺ = Et₃NH⁺)

entry	base	RCF₂	product	yield (%) vs 6a–d	yield (%) vs 1a–d
1	LiOH	$C_6H_5SCF_2CF_2$	**7a**	90	64
2	LiOH	$C_6H_5SCF_2$	**7b**	85	68
3	LiOH	$C_6H_5SO_2CF_2CF_2$	**7c**	77	52
4	LiOH	$C_6H_5SO_2CF_2$	**7d**	76	48
5	Et₃N	$C_6H_5SCF_2CF_2$	**2a**	82	58
6	Et₃N	$C_6H_5SCF_2$	**2b**	88	70

SCHEME 4. Postulated Mechanism of the Debenzylation Reaction
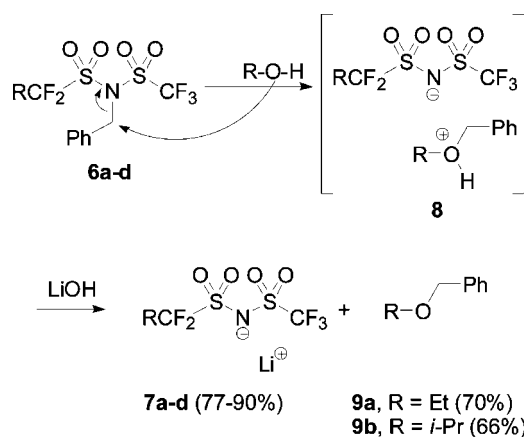
and palladium. Indeed, whereas **6a−d** were insoluble in ethanol, a complete dissolution was observed after 8 h and ¹⁹F NMR analysis confirmed that a reaction occurred. Finally, after addition of LiOH to the "solution" of **6a−d** in ethanol, the desired lithium salts **7a−d** were readily obtained (Table 3, entries 1−4). Although compounds **7a−d** were obtained as solids, it was not possible to measure their melting points due to their high sensitivity to moisture.

Actually, this deprotection reaction results from a nucleophilic substitution, at the benzylic center, of the sulfonimide group by the alcoholic oxygen (Scheme 4). This substitution is strongly favored by the presence of the electron-withdrawing fluorine atoms, which greatly enhances the nucleofugal character of the sulfonimide moiety. This mechanism has been experimentally confirmed by isolation of benzyl ethers **9a,b** after deprotection of **6a−d** in ethanol or 2-propanol.

This "one pot - 2 step" procedure was preferred to obtain sulfonimide salts with high purities. Indeed, small amounts of unidentified byproduct were observed when **6a−d** were directly treated with LiOH or LiOR. We assume that these undesired reactions were due to the nature of LiOH or LiOR which can abstract the benzylic protons or react on the sulfonyl groups of the *N*-benzylsulfonimides. In contrast, ethanol is a less basic and softer nucleophile, and thus, only nucleophilic substitution was observed.

It must be mentioned that few old papers already described the benzylation ability of *N*-benzyl-bis-trifluoromethanesulfon-imide.[16] Nevertheless, no attention was paid to the sulfonimide part which was considered as a useless byproduct. More

recently, DesMarteau et al. prepared new ionic liquids by using the methylating properties of *N*-methyl bis[(perfluoroalkyl)sul-fonyl]imides at 70 °C.[17] Nevertheless, they did not extend this method to benzylation which, owing to our present results, can be easily carried out at room temperature.

Our approach exhibits a wide scope since, in principle, it allows the preparation of numerous sulfonimides associated with a wide range of cations, depending upon the base used to neutralize the oxonium salt **8** (Scheme 4). Indeed, tertiary and quaternary ammonium sulfonimides can be also prepared from trialkylamines or ammonium hydroxides as bases. For example, triethylammonium sulfonimides **2a,b**, which are potential protonic electrolytes for fuel cells, were prepared from triethy-lamine (Table 3, entries 5 and 6).

The use of other tertiary amines and quaternary ammonium hydroxides are under study to get, respectively, new electrolytes for fuel cells or new ionic liquids.

Another advantage of our method can be pointed out when considering the final purification of lithium and ammonium sulfonimides: the only byproduct is a benzyl ether, which is easily separated from the desired salts. This constitutes a real progress over the previous procedures which require the separation of mixtures of organic salts.

Conclusion

In conclusion, we have developed an original approach, easy to scale up, to prepare new sulfonimide salts.[18] This method is based on two key steps: an efficient formation of a SO₂−N bond and an easy deprotection of a *N*-benzyl group. First, the reaction between sulfonyl fluorides and benzylamine avoids hydrolysis of the starting sulfonyl fluorides and provides *N*-benzylsulfona-mides in very good yields. Then, the introduction of the SO₂CF₃ part with triflic anhydride was found to proceed very well. Finally, *N*-deprotection was found to occur cleanly, under mild conditions, without any metal (cost and pollution advantages) and without any hydrogen (safety advantage). Moreover, this last step allows the preparation of sulfonimides associated with a wide range of cations. Therefore, this method was applied to the synthesis of a series of new lithium sulfonimides, which are potential electrolytes for lithium batteries, and extended to that of triethylammonium sulfonimides, which are potential electrolytes for fuel cells or potential ionic liquids. Data about the end-use properties of these new organic salts will be published in due time.

Experimental Section

Synthesis of *N*-Benzyl-2-(phenylsulfanyl)-1,1,2,2-tetrafluoro-ethanesulfonamide (4a). Freshly distilled benzylamine (4 mL, 37 mmol) was added at room temperature, under nitrogen, to a solution of **1a** (2.09 g, 7.2 mmol) in anhydrous 1,2-dichloroethane (20 mL). The mixture was stirred at 50 °C for 20 h (**1a** conversion monitored by TLC or ¹⁹F NMR). After the mixture was cooled to room temperature, aqueous HCl (10%) was added. The aqueous phase

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was extracted with CH_2Cl_2 and the organic layer dried over $MgSO_4$. Filtration and solvent evaporation left a residue which was purified by chromatography on silica gel (pentane to pentane/ethyl acetate 4/1). **4a** was obtained as a white solid (2.14 g, 77%).

Synthesis of *N*-Benzyl-*N*-(trifluoromethanesulfonyl)-2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonamide (6a). Diisopropylethylamine (70 μL, 0.4 mmol) was added under nitrogen to a solution of **4a** (0.15 g, 0.4 mmol) in anhydrous CH_2Cl_2 (2.5 mL). The reaction was cooled to -10 °C, and triflic anhydride (100 μL, 0.6 mmol) was added. The mixture was stirred for 30 min at this temperature and then for 1 h at room temperature (reaction monitored by ^{19}F NMR in $CDCl_3$). Solvent and volatile byproduct were evaporated under reduced pressure. The residue was refluxed in pentane, and before cooling to room temperature, the pentane fractions were collected. This operation was repeated several times. Evaporation of the combined pentane fractions left **6a** as a white solid (0.19 g, 92%).

Synthesis of Lithium *N*-(Trifluoromethanesulfonyl)-2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonamide (7a). A suspension of **6a** (0.51 g, 1 mmol) in ethanol (5 mL) was stirred at room temperature for 8 h until clear. Then, $LiOH \cdot H_2O$ (42 mg, 1 mmol) was added, and the reaction mixture was stirred overnight. After evaporation of the solvent, the residue was dissolved in ether and filtered over Celite. Evaporation of the filtrate gave a solid which was washed several times with pentane to deliver **7a** as a hygroscopic white solid (0.39 g, 90%).

Supporting Information Available: General methods, experimental procedures, compound characterization, and copies of the NMR spectra data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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