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One-pot Synthesis of Aryl- and Alkyl *S*-Perfluoroalkylated *NH*-Sulfoximines from Sulfides

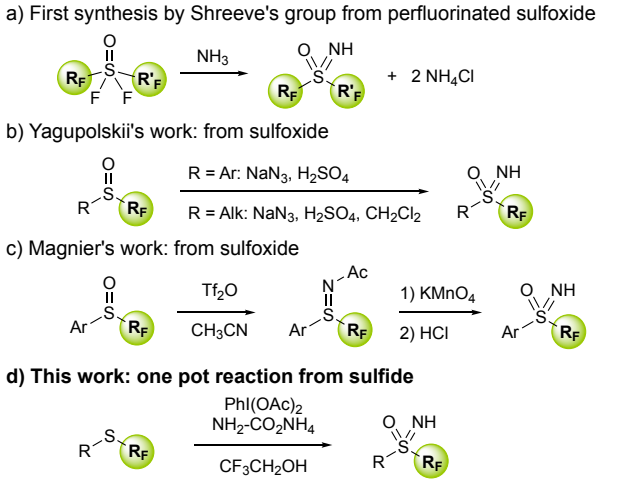
Slim Chaabouni,[a] Jean-François Lohier,[a] Anne-Laure Barthelemy,[b] Thomas Glachet,[a] Elsa Anselmi,[b] Guillaume Dagousset,[b] Patrick Diter,[b] Bruce Pégot,[b] Emmanuel Magnier*[b] and Vincent Reboul*[a]

Abstract: A general efficient one-pot synthesis of *S*-perfluoroalkylated *NH*-sulfoximines from sulfides has been developed using PIDA and ammonium carbamate. Remarkable rate enhancement with trifluoroethanol was observed, presumably due to H-bonding effects. These mild and metal-free conditions are compatible with $-CH_2F$, $-CFCl_2$, $-CF_2H$, $-CF_2Br$, $-C_4F_9$ and $-CF_3$ groups, in both the alkyl- and aryl series. Based on a ^{19}F NMR analysis, a λ^6-acetoxysulfanenitrile intermediate was proposed.

Since their discovery in 1950 by Bentley and Whitehead,[1] *NH*-sulfoximines, the mono-aza analogues of sulfones, have attracted much attention as illustrated by their wide application in organic synthesis, and their promising properties for medicinal chemistry.[2] The interest in the *S*-fluorinated sulfoximines has grown in recent years, owing to their very peculiar properties.[3] Shibata first demonstrated their ability to transfer the perfluoroalkyl group to nucleophiles, and was followed by others.[4] Fluorinated sulfoximines can furthermore act as nucleophiles as performed by Hu,[5] or radical transfer agents.[6] They are also employed as *ortho*-directing groups,[7] building blocks for liquid crystals[8] and as powerful electron withdrawing entities.[9] However, the principal drawback to their development is still the lack of general preparation methods. If remarkable efforts were made in the recent past to develop efficient syntheses of non-fluorinated sulfoximines, it is important to point out that these methodologies can hardly be transposed to the fluorinated series.[10] This is mainly explained by the poor nucleophilicity of the sulfur atom. Bolm confirmed the ineffective nitrene transfer to phenyl trifluoromethyl sulfide and its corresponding sulfoxide and thus developed a three step synthesis of *N*-protected trifluoromethyl sulfoximines.[11] The same tendency was observed by Luisi and Bull during the metal-free nitrene transfer to 4-bromophenyl trifluoromethyl sulfoxide.[12] The first synthesis of fluorinated *NH*-sulfoximines was described by Shreeve's group by using sulfur oxydifluorides and ammonia.[13] Unfortunately, this method was limited to the bis(perfluoroalkyl) series (Scheme 1a). To date, the most straightforward synthesis is the reaction (by the combination of sodium azide in sulfuric acid or oleum) first reported by Yagupolskii's group in 1984 (Scheme 1b).[14] By adaptating these conditions (dilution with dichloromethane or chloroform), this methodology could be applied to a fluoromethyl group[4b] as well as in the aliphatic series.[15] However, this reactions remained difficult to handle due to the explosiveness and toxicity of these reagents. To circumvent this issue, Magnier reported a safer three steps synthesis starting from sulfoxides through a Ritter type reaction (mediated by Tf_2O and acetonitrile) which allowed the synthesis of *NH*-sulfoximines after oxidation and subsequent deprotection of the nitrogen (Scheme 1c).[16] This procedure also suffers from drawbacks: its inefficiency in the *S*-alkyl series as well as with *S*-fluoromethyl chains.

Regarding the growing interest for *S*-perfluoroalkyl sulfoximines, there is an urgent need to tackle the limitations previously mentioned, as well as a common one: the use of a sulfoxide as the starting material. In the context of an exponential growth of methodologies to prepare the SCF_3 moiety,[17] the use of this group as a substrate would be a fantastic advantage.

We report herein a general, safe, one-pot and metal-free preparation of aryl- and alkyl *NH*-sulfoximines from the corresponding sulfides and applicable to a wide range of fluorinated chains (Scheme 1d). A mechanistic investigation of this reaction was also performed.



Scheme 1. Preparation of *NH*-fluorinated sulfoximines

The group of Reboul recently developed an efficient synthesis of non-fluorinated *NH*-sulfoximines from sulfides using phenyliodine diacetate (PIDA) and ammonium carbamate (AC). with methanol as the solvent.[18] However, when the reaction was

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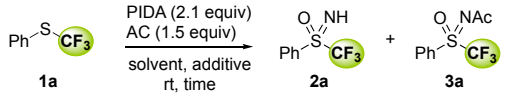
conducted in this solvent using trifluoromethyl phenyl sulfide **1a**, only traces of the desired *NH*-sulfoximine **2a** were detected by ^{19}F NMR analysis of the crude product and sulfide **1a** was recovered (Table 1, entry 1). We reasoned that increasing the electrophilicity of the hypervalent iodine species could enhance the reactivity. With $BF_3.Et_2O$, described as an efficient activator,[19] no conversion was observed (entry 2). We next investigated the use of highly polar and strong hydrogen-bond donating solvents.[20] Hexafluoro-isopropanol (HFIP) led to complete conversion but also to a messy crude mixture (Table 1, entry 3). In contrast, we were delighted to find that trifluoroethanol (TFE) led to the formation of sulfoximine **2a** in 52% yield (Table 1, entry 4). Adding nucleophilic additives such as methanol or water to the reaction mixture (Table 1, entries 5-7) did not improve the yield.

Table 1. Optimization of reaction conditions using sulfide **1a**



1a **2a** **3a**

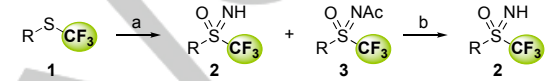
Entry	Solvent, additive	Time [h]	Conversion; **2a**/**3a** ratio [%][a]	Yield of **2a** [%][a]
1	MeOH	3	7; nd	traces
2	CH_2Cl_2, $BF_3.Et_2O$	3	0; nd	nd
3	HFIP	3	97; nd	traces
4	TFE	3	59; 88/12	52
5	1:1 MeOH/TFE	3	30; 90/10	27
6	1:9 MeOH/TFE	3	52; 88/12	47
7	1:9 H_2O/TFE	3	53; 88/12	46
8	TFE	6[b]	85; 88/12	75
9	TFE	3+3[c]	100; 88/12	83[d]
10	TFE, PIFA[e]	3	0; nd	nd

[a] Estimated by ^{19}F NMR with $PhOCF_3$ as internal standard. [b] PIDA (3.1 equiv) and AC (2.5 equiv) were used. [c] Addition of PIDA and AC (1 equiv) to the reaction mixture after 3 h. [d] Isolated yield of **2a** after acid hydrolysis (HCl/CH_3CN). [e] PIFA was used instead of PIDA.

When the reaction time was extended to 6 h with the utilization of an excess of PIDA/AC (3 equiv/2.5 equiv), the conversion rose to 85% (Table 1, entries 8). Full conversion was achieved by adding 1 equiv of each reagent after 3 h (Table 1, entry 9). The use of TFE systematically delivered a constant ratio of molecules **2a/3a** (see the mechanistic discussion). To avoid tedious separation, the crude mixture was directly treated with HCl 6 M in acetonitrile in order to deprotect **3a** (full conversion after 12 h).[4e] Using those optimized conditions, sulfoximine **2a** was isolated in 83% yield.[21] However, when phenyliodine ditrifluomethylacetate (PIFA) was used instead of PIDA, no reaction occurred (Table 1, entry 10). With these conditions in hand, the scope of the reaction was evaluated in the trifluoromethyl series (Table 2).

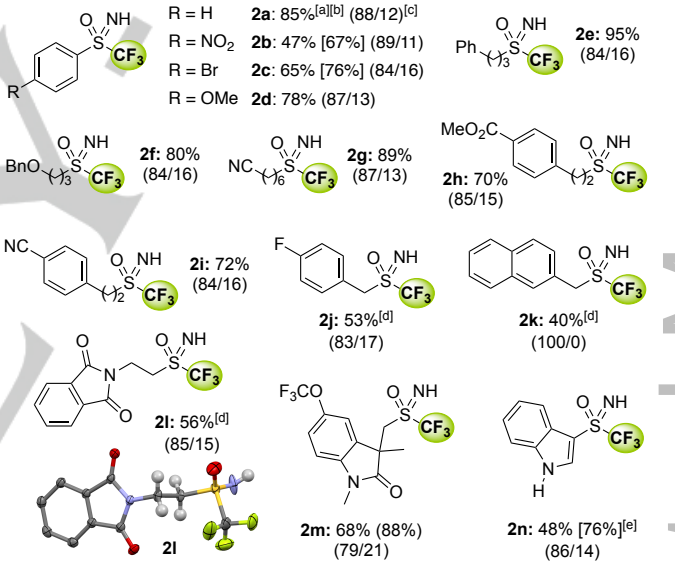
The scalability of the reaction was first demonstrated by conducting the reaction with **1a** on a 12 mmol scale without erosion of the yield. With electron withdrawing groups on the phenyl group, the conversion was lower and the yields dropped to 47% for **2b** and 65% for **2c**. On the other hand, the phenylsulfide **1d** bearing a 4-methoxy substituent, led to an excellent yield of 78% (**2d**). The same reaction conditions were then applied to the challenging alkyl series. We were delighted to obtain very high yields starting from sulfides containing an alkyl chain (with 2, 3 or 6 carbon atoms) ending in a phenyl (**2e;** 95%), benzyloxy (**2f;** 80%), cyano (**2g;** 80%), phenylester (**2h;** 70%) or phenylcyano (**2i;** 72%) group. However, with benzylic sulfide (**2j** and **2k**) groups, the acid hydrolysis led to decomposition of both sulfoximines. Consequently, this step was not performed and moderate yields were obtained. Sulfoximine **2n**, bearing an *N*H-indole group, was also obtained in 48% yield from *N*Boc-indole protected sulfide.

Table 2. Reaction scope with various aryl- and alkyl trifluoromethyl sulfides[a,b]



1 **2** **3** **2**

a: PIDA (2,1 equiv), AC (1.5 equiv), TFE, rt, 3 h then PIDA (1 equiv), AC (1 equiv), 3 h
b: HCl, CH_3CN, rt, 12 h



[a] Isolated yields. Full conversion was almost always obtained, otherwise indicated in square brackets. [b] Reaction performed on 12 mmole scale. [c] Ratio of *NH* and *N*Ac sulfoximines measured by ^1H or ^{19}F NMR analysis of the crude mixture indicated in brackets. [d] Isolated yield without acid hydrolysis. [e] The NBoc indole deprotection occurred during the acid hydrolysis at 80°C.

As a first progress status, our methodology allowed a mild one-pot transformation of alkyl and aryl trifluoromethyl thioethers into the corresponding sulfoximines. In light of these results, we anticipated that our sulfoximination reaction could be applied to other perfluoroalkyl series (Table 3). Sulfoximines bearing a nonafluorobutyl group were indeed prepared in both the alkyl (**4c**) and aryl series (**4a**, **4b**[22]) with good yields. With sulfides bearing a CF_2Br group, excellent yields were obtained with a phenyl (**5a**; 87%), a tolyl (**5b**; 76%) or a 4-$MeOC_6H_4$ (**5c**; 86%) group as well as with an aliphatic substrate (**5d**, 49%). X-ray structure of **5b** reveals an *anti* staggered conformation between the bromine and the tolyl group.

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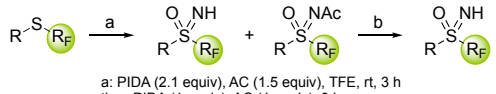
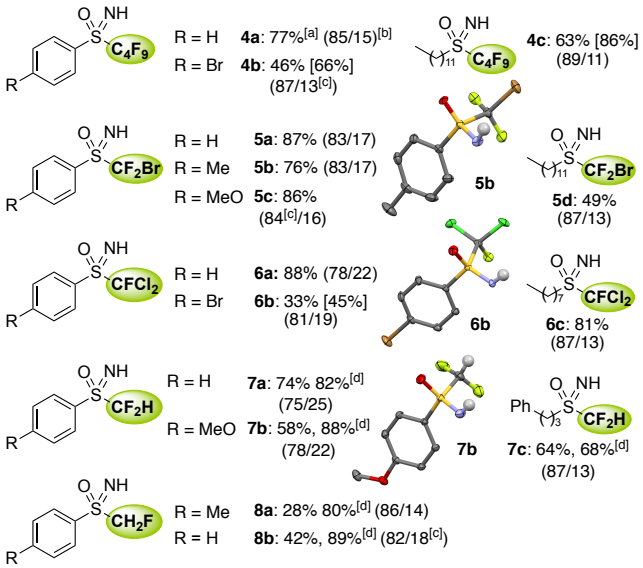
Table 3. Reaction scope with various aryl- and alkyl fluorinated sulfides[a,b]



a: PIDA (2.1 equiv), AC (1.5 equiv), TFE, rt, 3 h
then PIDA (1 equiv), AC (1 equiv), 3 h
b: HCl, CH_3CN, rt, 12 h



[a] Isolated yields. Full conversion was almost always obtained, otherwise indicated in square brackets. [b] Ratio of NH and NAc sulfoximines measured by ^1H or ^{19}F NMR analysis of the crude mixture indicated in brackets. [c] X-Ray was obtained. [d] Reaction performed in MeOH.

Monofluoro dichloro thioethers proved also to be efficient substrates as illustrated by the synthesis of aryl (**6a, 6b**) and alkyl sulfoximines (**6c**). The reactivity with the challenging difluoromethyl and fluoromethyl moieties was more surprising. The difluorinated substrates gave rise to the *S*-aryl sulfoximines **7a-b** and *S*-alkyl sulfoximine **7c** with good yields. Quite unexpectedly the latter was improved with methanol as the solvent. This result was even more pronounced with the fluoromethyl phenyl thioether. With TFE, a moderate yield of 42% of sulfoximine **8a** was obtained whereas with methanol, the sulfoximines **8a** and **8b**[22] were isolated in excellent yields of 80% and 89% respectively. These last conditions, which were already described for the non-fluorinated series,[18] were only efficient for these two *S*-difluoromethyl and *S*-monofluoromethyl substrates with an emphasis for the latter.[23] In other cases, TFE is essential. This last remark suggests a different pathway between the non-fluorinated thioethers and the perfluoroalkylated ones. Consequently, special attention was paid to the reaction mechanism.

Monitoring of the reaction by ^{19}F NMR analysis (in TFE at 0°C) as well as by mass spectrometry was undertaken (Figure 1). The (4-methoxyphenyl) difluoromethyl thioether was chosen as the model substrate because of its peculiarly remarkable NMR signals. Both expected sulfoximines, **NH-7b** and **NAc-7b**, possess two diastereotopic fluorine atoms. After one minute of reaction, we thus observed the rapid formation of **NH-7b** (AB part of ABX system in blue at –121.8 and –119.3 ppm) and **NAc-7b** (AMX system in green, 2 dd at –115.4 and –122.7 ppm) sulfoximines (Figure 1). We also observed a doublet (purple, at –118.2 ppm) and another AMX system (2 dd in red at –114.2 and –120.1 ppm). These latter signals gradually disappeared over time (Figure 1, top) in favour of the two sulfoximines. Close examination of the HRMS spectrum of the crude product, revealed a mass corresponding to the sulfoximine **10** bearing a [I^+Ph] on the nitrogen atom. The structure of compound **10** was undoubtedly confirmed by mixing sulfoximine **NH-7b** with PIDA. The CF_2H group in ^{19}F NMR spectrum appeared as a doublet (surprisingly the two fluorine atoms are magnetically equivalent at –118.2 ppm). Consequently, we assigned this purple signal to the sulfoximine **10**. This compound **10** is very sensitive to hydrolysis and slowly led to the corresponding *NH*-sulfoximine **7b**. Its formation can also explain the need for an excess of PIDA. The last species detected by NMR showed a AMX system (red colour in figure 1). Its concentration remains low and stable during the first 5 hours before final disappearance.

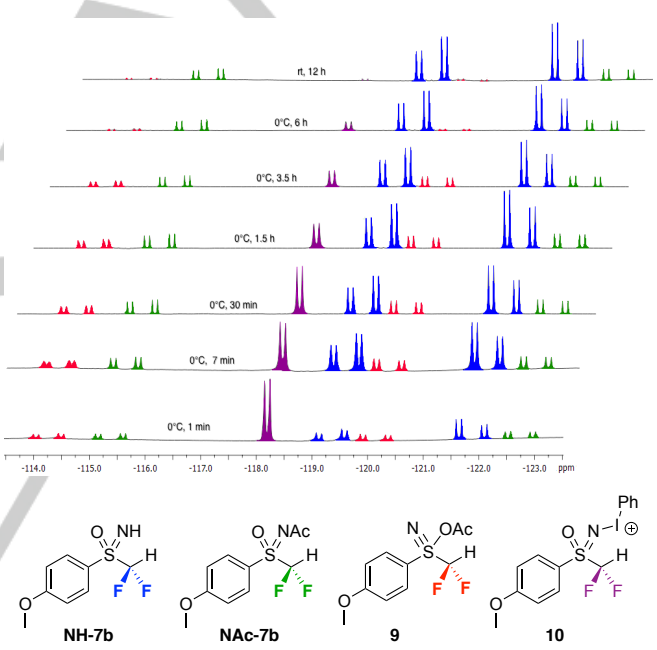


Figure 1. ^{19}F NMR spectra ($CDCl_3$, 564 MHz, –20°C) of reaction mixture over time, selected region (δ = –113 to –124 ppm).

This intermediate possess an asymmetric sulfur atom. Based on our previous experience,[18] its structure was assigned to sulfanenitrile **9** and allowed us to propose the following mechanism. It starts with the initial formation of an activated nitrene, mediated by TFE, able to react with perfluoroalkylthioethers (Scheme 2). As this species has a very short life time, no observation by NMR analysis was successful. We postulate that a H-bonded adduct between the TFE and PIDA led to the formation of the $[PhI(OAc)]^+$ cation **A**. In the presence of ammonia, nitrene **B** should be formed, as described by Luisi and Bull[24] and by Reboul,[18] in the non-fluorinated series.[25] The TFE would also be involved in the formation of the activated nitrene [PhI^+N] **C** through H-bonding. The reaction of the latter with the sulfur atom gives rise to a sulfilimine **D**, undetected by

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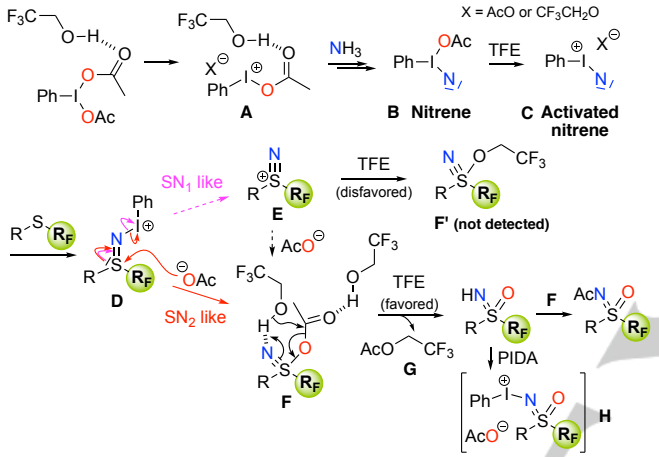
NMR analysis. The nucleophilic attack of an acetate anion on this short lived species (S_N2 type reaction, Scheme 2, red arrows) delivers the observed sulfanenitrile intermediate **F**. Subsequent attack of TFE on the latter account for the formation of the *NH*-sulfoximine as proved by the presence of the trifluoroethanolacetate **G**[26] (observed in the crude mixture). Last, the *NH*-sulfoximine can react either with the PIDA (formation of **H**) or with the sulfanenitrile **F** according to the isolated mixture of NH and NAc sulfoximines. Although not proved by our experimental observations, a second pathway cannot be totally ruled out. The formation of a thiazynium **E** should be possible *via* a S_N1 like mechanism from sulfilimine **D** (Scheme 2, purple arrows), as proposed by Yoshimura.[27] Considering the poor nucleophilicity of trifluoroethanol, the thiazynium **E** would evolve into sulfanenitrile **F** instead of **F'**.



Scheme 2. Proposed mechanism.

In summary, we have reported the first direct synthesis of fluorinated *NH*-sulfoximines from sulfides in both the alkyl and aryl series. A diverse set of important functional groups were well tolerated. Remarkable reactivity enhancement with TFE was observed. In agrochemical and medicinal chemistry, the use of fluorinated sulfoximines has been neglected for a long time[28] and we expect this methodology will be used in order to increase chemical diversity. Further investigations to expand the reactivity of such species are also in progress in our laboratories.

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Keywords: fluorinated NH-sulfoximines • PIDA • iodonitrene • thiazynium • λ^6–sulfanenitrile

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[21] Sulfoximine **2a** was also obtained from the corresponding sulfoxide but in a lower yield of 51% using the optimized conditions.

[22] The X-ray structure of the corresponding N-Ac sulfoximine was obtained. See Supporting Information.

[23] We rationalized theses results considering the poor nucleophilicity of the sulfur atom when a trifluoromethylthio group is present.

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[25] The formation of the iodonitrene (**B** or **C)** is not observed when PIFA and ammonium carbamate (or ammonia) were mixed in MeOH (no formation of N_2).

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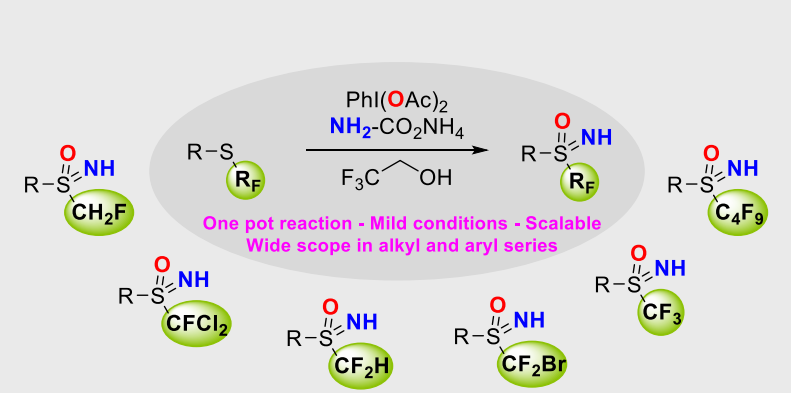

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