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Self-Immolative Reduction of Trifluoromethyl Sulfoxides Promoted by Trifluoromethanesulfonic Anhydride

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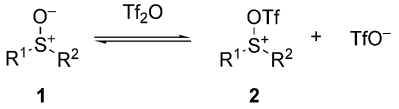
Keywords: Reduction / Anhydrides / Fluorine / Reaction mechanisms / Sulfur

We investigated the behavior of the extensively used system trifluoromethanesulfonic anhydride/sulfoxide in the absence of any added nucleophilic species. We show here, with the help of ^{19}F NMR spectroscopy, that in the case of trifluoromethyl sulfoxides this results initially in the net reduction of the sulfoxide to a sulfane. We propose a mechanism involving sulfoxide itself as the reducing agent.

Introduction

Trifluoromethanesulfonic anhydride (triflic anhydride, Tf_2O) is a reagent extensively used in organic chemistry that allow numerous useful synthetic transformations.[1] This strongly electron-deficient compound is able to react with very weakly nucleophilic functionalities to provide highly activated species.[2] In the particular case of sulfoxides **1** as nucleophilic components, this property has been fruitfully used for the generation of efficient glycosylation agents,[3] promoters for sulfonium salts[4] and sulfilimines[5] synthesis, as well as mild oxidizing reagents.[6] The pivotal species in all these applications may be presumed to be activated form **2** of the sulfoxide [Equation (1)].[7]

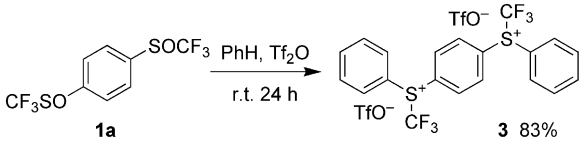


1 **2** (1)

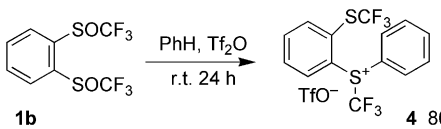
In most cases, activated intermediate **2** is trapped in situ, at low temperature, by a nucleophilic reagent. However, what happens to this species in the absence of any added nucleophilic component is unclear. It has been reported in one instance that decomposition of a mixture of triflic anhydride and phenyl benzenethiosulfinate occurs at temperatures above –60 °C,[3c] but the nature of the products formed was not disclosed.[8] Analogous experiments with trifluoroacetic anhydride instead of triflic anhydride afforded diphenyl disulfide and phenyl benzenethiosulfonate by an apparent disproportionation reaction.[9]

Results and Discussion

Interestingly, while studying the preparation of sulfonium salts from trifluoromethyl sulfoxides in the presence of trifluoromethanesulfonic anhydride under current standard conditions,[4b] Shreeve uncovered an unexpected reduction process.[10] Whilst 1,4-bis(trifluoromethyl) phenyl sulfoxide (**1a**) was transformed into expected bis(sulfonium) salt **3** [Equation (2)], its corresponding 1,2-isomer **1b** suffered reduction of just one sulfoxide group resulting in monosulfonium salt **4** [Equation (3)].



1a **3** 83% (2)



1b **4** 80% (3)

One step further, in a related study, we ourselves showed that the presence of triflic anhydride alone was sufficient to observe a cognate partial reduction of phenyl trifluoromethyl sulfoxide (**1c**), leading ultimately to trifluoromethylsulfanyl sulfonium salt **5a** [Equation (4)].[4c]

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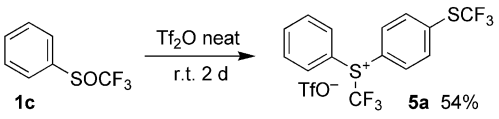


(4)

These latter results strongly suggest the intervention of a reduction process in such systems. Triflic anhydride has been noticed to act as an oxidizer in some particular cases,[1,11] but its reducing ability remained to be demonstrated. In the cases mentioned above, the exact nature of the reducing agent and the mechanism of this intriguing reduction process remain to be elucidated. In this paper we aim to shed some light on both aspects of this reaction by using the unique capacity of fluorine to act as a convenient probe in complex reaction mixtures by the use of ^{19}F NMR spectroscopy.

Our study focused on the seemingly simpler reaction described in Equation (4). In this case, the only reactants present at the beginning of the reaction were sulfoxide **1c** and triflic anhydride. In order to dismiss any influence of light[12] or of the glassware, this reaction was also successfully performed in the dark and in an all-Teflon apparatus.

The scope of this reaction is not limited to phenyl trifluoromethyl sulfoxide (**1c**) itself,[13] as it can tolerate aromatics substituted with electron-donating methyl groups. With *ortho*-tolyl trifluoromethyl sulfoxide, after 7 d reaction unique sulfonium salt **5b** was isolated in 48% yield and shown to possess the structure *S*-trifluoromethyl-*o*-tolyl-4-(*o*-tolylthio)sulfonium by a combination of NMR spectroscopy experiments and estimations of ^{13}C NMR chemical shifts using substituents increments.[14,15] *meta*-Tolyl trifluoromethyl sulfoxide gave an inseparable mixture of sulfonium salts **5c** and **5d** (ratio 85:15) in 81% yield after 8 d reaction. Assignment of structure **5d** for the minor isomer was greatly helped by the existence of a coupling constant (J = 1.7 Hz) between the fluorine atoms of the trifluoromethyl sulfane group and the trifluoromethyl sulfonium group. suggesting close spatial proximity (through-space coupling).[16] Conversely, a small coupling constant (J = 0.8 Hz) is also observed between the fluorine atoms of the trifluoromethyl sulfonium group and the carbon atom of the methyl group in major isomer **5c**.

Despite a strongly exothermic reaction, no sulfonium salt could be isolated with *para*-tolyl sulfoxide. In this particular case, we believe that participation of the *para*-methyl group occurs upon activation of the sulfoxide by triflic anhydride.[5b]

By contrast, only a trace amount of sulfonium salt was observed upon reaction of chlorophenyl derivatives irrespective of their substitution pattern (*ortho*, *meta*, or *para*) after an extended reaction period (1–2 months).

In order to gain some insight into the reaction process, the reaction between **1c** and Tf_2O in a sealed tube was followed by ^{19}F NMR spectroscopy by using a solution of sodium trifluoromethanesulfinate in D_2O contained in an internal capillary for reference (δ = –88.0 ppm) and lock purposes (Figure 1).

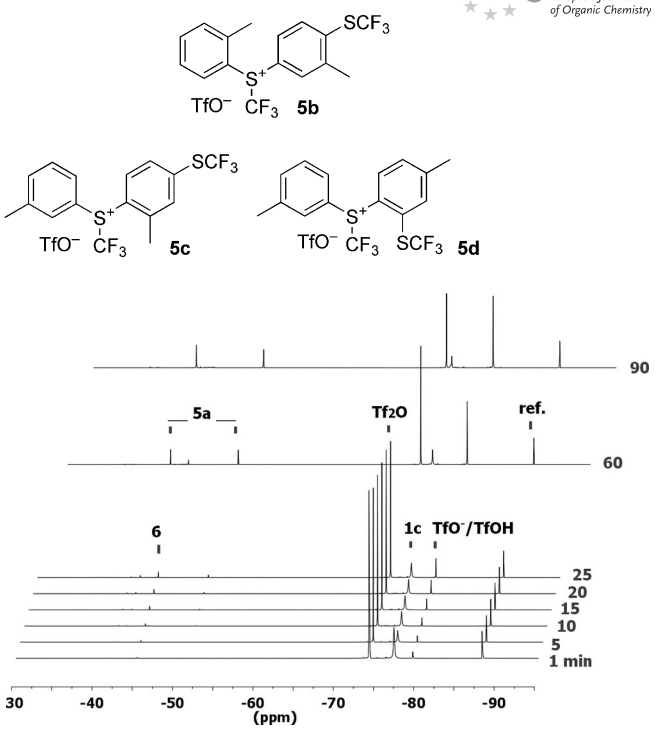
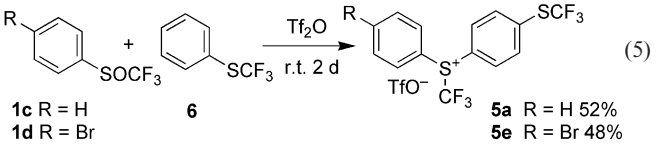


Figure 1. Temporal stacked plot of the ^{19}F NMR spectra showing the progress of the reaction between **1c** and Tf_2O.

No phenyl trifluoromethyl sulfone could be detected (ref.[4b] δ = –78.8 ppm in $CDCl_3$, δ = –81.0 ppm in our solvent system[17]), ruling out a simple disproportionation reaction of sulfoxide to sulfane and sulfone. This observation is in line with the yields over 50%, based on sulfoxide, achieved in the work of Shreeve[10] as well as in our own study [Equations (3) and (4)].[4c]

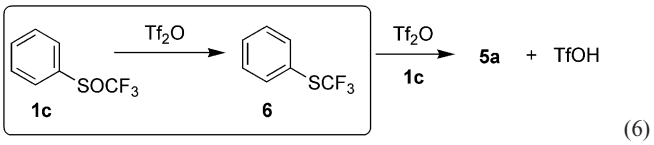
One can also notice the presence of phenyl trifluoromethyl sulfane (δ = –45.0 ppm) **6** [Equation (5)] in the ^{19}F NMR spectra at the early stage of the reaction. This compound disappears further in favor of sulfonium salt **5a**.

We are thus considering that the formation of sulfonium salt **5a** occurs through prior reduction of sulfoxide **1c** to sulfane **6**, which is consumed by usual reaction with **1c** upon activation of the latter by triflic anhydride. To support this hypothesis, we have shown, in independent experiments, that either sulfoxide **1c** or **1d** reacted readily with sulfane **6** by using the Shreeve protocol[4b] [Equation (5)] to give the corresponding sulfonium salt **5a** (52% yield) or **5e** (48% yield), respectively. This demonstrates that sulfane **6** is nucleophilic enough to react with the activated form of the sulfoxide [Equation (5)].



(5)

On the basis of the previous considerations, Equation (4) may then conceptually be broken down into two consecutive events as indicated in Equation (6).

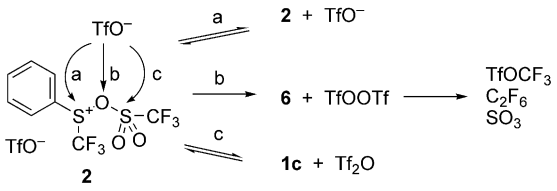


(6)

An initial reduction of sulfoxide **1c** to sulfane **6** (highlighted) [Equation (6)], followed by a more conventional reaction between sulfane **6** and sulfoxide **1c** activated by triflic anhydride should lead to the formation of sulfonium salt **5a**. We are thus now faced with the highlighted part of Equation (6), the reduction of sulfoxide **1c** to sulfane **6** in the presence of triflic anhydride.

By analogy with Equation (1), one can speculate that some kind of activation of sulfoxide **1c** occurs prior to its reduction to sulfane **6**. The best candidate for this purpose should be triflic anhydride, but activation of sulfoxide **1c** can also occur by protonation at oxygen by triflic acid. This acid may either be released during formation of sulfonium salt **5a** [Equation (6)] or upon hydrolysis of Tf_2O by adventitious presence of water. It should be considered however that upon mixing sulfoxide **1c** with triflic acid alone we only noticed a shift in the ^{19}F NMR spectrum of **1c** perhaps indicative of a protonation equilibrium (δ = –66.7 ppm in pure TfOH as solvent with external sodium triflinate as reference, $\Delta\delta$ ca –10 ppm compared to solution in Tf_2O).[18] Despite this apparent protonation, no reaction occurs even in the presence of benzene as nucleophilic agent more able to trap any cationic species in the reaction medium. This rules out any direct participation of triflic acid in the present process.

As explained in the introduction, sulfoxides are known to react reversibly with triflic anhydride to give activated sulfoxide species **2** [Equation (1)]. In this case, species **2** may conceptually react with nucleophiles[19] at three different centers: cationic sulfur (a), oxygen (b), or sulfone (c, Scheme 1).



Scheme 1. Triflate as nucleophile.

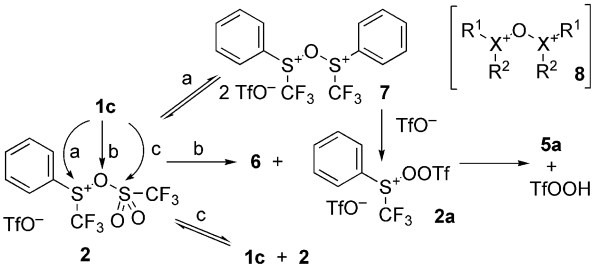
Direct attack at the trifluoromethyl group can be dismissed because of the very effective shielding of the carbon atom effected by the presence of the fluorine atoms.[20] During the reduction of sulfoxide **1c** to sulfane **6**, attack at the aromatic nucleus can also be dismissed because formation of sulfane **6** occurs without substitution of the aromatic ring.

Only two nucleophilic species are present in the medium: the triflate anion and sulfoxide **1c**, giving at first six combinations of nucleophiles and reactive centers.

If we first consider the triflate anion as the nucleophilic species, attack at center a is degenerate (Scheme 1), intermediate **2** being formed again, whereas attack at center c will revert one step further, giving triflic anhydride along with sulfoxide **1c**. Attack at oxygen center b seems more interesting and should lead to, besides sulfane **6**, to known bis(trifluoromethylsulfuryl) peroxide (TfOOTf).[21] However, neither this compound (δ = –72.4 ppm) nor its thermal decomposition products[22] hexafluoroethane (δ = –89.1 ppm) and trifluoromethyl trifluoromethanesulfonate (δ = –76.2 and –55.6 ppm; $J_{F,F}$ = 3.4 Hz)[21,23] could be detected in our NMR spectroscopy study.

In fact, the oxygen atom of sulfoxide **1c** may be presumed to be the most nucleophilic center in this medium. The clear dichotomy between the behavior of *ortho* **1b** and *para* bis(trifluoromethyl) **1a** sulfoxides observed by Shreeve[10] suggests that a close spatial proximity of two fluorinated sulfoxide functionalities are necessary for the reduction to occur. In our case, whereas the reaction must be intermolecular, this close proximity may be insured by the high concentration of the sulfoxide in the medium in the absence of any solvent (mol fraction of sulfoxide ca. 0.3). To support this view, a reaction performed without solvent took about 2 d to reach completion, whereas in the presence of dichloromethane (mol fraction ca. 0.03) the same reaction was completed only after 1 month.

Again, intermediate **2** may react with sulfoxide **1c** at one of the three centers shown in Scheme 2. Attack at center c is degenerate. Attack at center a (reversible) should give rise to new dicationic intermediate **7**. Some dicationic intermediates **8** (Scheme 2) related to **7** are known (and sometimes isolable) when the cationic center X is carbon (stabilized by nitrogen groups), nitrogen, phosphorus, or arsenic, but to the best of our knowledge, they have never been described (or have been overlooked) for X = S.[1] Whatsoever, either attack of triflate on oxygen in intermediate **7** or more likely considering the better nucleophilicity of sulfoxide, attack of sulfoxide **1c** at center b on intermediate **2** should give rise to the same apparent reaction, formation of sulfane **6** and of peroxy intermediate **2a** (Scheme 2).[24]



Scheme 2. Sulfoxide **1c** as nucleophile.

Intermediate **2a** is nothing but a more-oxidized form of activated sulfoxide intermediate **2**, and as such, it is susceptible to react with any nucleophilic species present in the medium (in particular **6**) releasing the peroxytriflate anion ($TfOO^-$). Peroxytrifluoromethanesulfonic acid was used as a powerful oxidant, better than trifluoroperoxyacetic

acid,[25] but quite poorly characterized by ^{19}F NMR spectroscopy (δ = –77.6 ppm)[26] as a thermally unstable compound and better used as an in situ formed reagent.[27] The poor thermal stability and presumed rapid decomposition giving back trifluoromethanesulfonic acid precluded any detection in our NMR spectroscopy study. Efforts devoted to demonstrate the transient presence of this peroxide by the introduction in the reaction medium of an oxidizable species (*p*-bromotrifluoromethylsulfane or an alkene) failed to give any detectable corresponding oxidized compound.

Conclusion

In summary, whatever the nucleophilic species involved, only attack at oxygen (path b) may result in the formation of sulfane **6**. Although seemingly less favorable, this attack may be successful because reactions at the other possible centers are either degenerate or reversible. In both cases, an unstable intermediate will be formed, which should either have been detected by NMR spectroscopy (TfOOTf), at least by its decomposition products, or have escaped any attempts to detect it ($TfOO^-$, TfOOH) because of its very fast decomposition into species already present in the reaction medium (TfO^-, TfOH). In fact, our results suggests that reduction of sulfoxide **1c** to sulfane **6** under our conditions follows partially the usual reduction route of sulfoxides,[28,29] with conventional prior activation, in the present case with triflic anhydride, followed by a less conventional reaction with sulfoxide **1c** itself (Scheme 2, path b).

Experimental Section

Typical Procedure for the Preparation of Sulfonium Salts from Sulfoxides and Triflic Anhydride: A solution of trifluoromethyl sulfoxide **1** (2.58 mmol) in trifluoromethanesulfonic anhydride (2.1 mL, 12.8 mmol, 5 equiv.) was stirred under an atmosphere of argon for 2 to 9 d until total consumption of sulfoxide **1** (followed by ^{19}F NMR spectroscopic analysis of aliquots). The reaction mixture was poured onto iced water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). Extracts were washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. Sulfonium **5** was isolated by flash chromatography of the residue (SiO_2; CH_2Cl_2/MeOH, 90:10).

[3-Methyl-4-(trifluoromethylsulfanyl)phenyl]-(*o*-tolyl)-*S*-trifluoromethylsulfonium Trifluoromethanesulfonate (5b): Yield: 330 mg (48%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 2.1 Hz, 1 H, 2′-H), 8.07 and 8.06 (AB system: dd, *J* = 8.7, 2.1, 1 H, 6′-H and d, *J* = 8.7 Hz, 1 H, 5′-H), 7.93 (br. d, *J* = 8.2 Hz, 1 H, 6-H), 7.80 (td, *J* = 7.6, 1.4 Hz, 1 H, 4-H), 7.69 (td, *J* = 7.9, 1.8 Hz, 1 H, 5-H), 7.62 (dd, *J* = 7.8, 1.9 Hz, 1 H, 3-H), 2.83 (s, 3 H, 2-Me), 2.64 (s, 3 H, 3′-Me) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –40.8 (s, 3 F, SCF_3), –48.7 (s, 3 F, S^+CF_3), –79.0 (s, 3 F, $CF_3SO_3^-$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.3 (q, *J* = 0.9 Hz, 1 C, 3′-C), 145.2 (s, 1 C, 2-C), 138.5 (q, *J* = 1.1 Hz, 1 C, 5′-C), 137.3 (s, 1 C, 4-C), 135.6 (q, *J* = 2.1 Hz, 1 C, 4′-C), 135.0 (q, *J* = 1.2 Hz, 1 C, 2′-C), 134.2 (s, 1 C, 3-C), 131.4 (q, *J* = 1.5 Hz, 1 C, 6-C), 130.3 (s, 1 C, 5-C), 129.9 (q, *J* = 309.5 Hz, 1 C, SCF_3), 129.9 (q, *J* = 1.5 Hz, 1 C, 6′-C), 123.5 (q, *J* = 328.8 Hz, 1 C, S^+CF_3), 120.8 (q, *J* = 320.4 Hz, 1 C, $CF_3SO_3^-$), 119.0 (s, 1 C, 1-C), 115.8 (s, 1 C, 1′-C), 21.4 (s, 1 C, 3′-Me), 20.4 (s, 1 C, 2-Me) ppm. HRMS: calcd. for $C_{16}H_{13}F_6S_2$ 383.0363; found 383.0345 (δ = –4.7 ppm).

[2-Methyl-4-(trifluoromethylsulfanyl)phenyl]-(*m*-tolyl)-*S*-trifluoromethylsulfonium Trifluoromethanesulfonate (5c): Yield: 560 mg (81%). Major isomer 85% of the mixture. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.11 (br. s, 1 H, 1-H), 8.03 (m, 1 H, 5-H), 7.96 (d, *J* = 8.7 Hz, 1 H, 5′-H), 7.85 (dd, *J* = 8.7, 2.2 Hz, 1 H, 4′-H), 7.78 (br. s, 1 H, 2′-H), 7.68–7.76 (m, 2 H, 3-H and 4-H), 2.87 (s, 3 H, Me), 2.52 (s, 3 H, Me) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –40.4 (s, 3 F, SCF_3), –47.9 (s, 3 F, S^+CF_3), –78.5 (s, 3 F, $CF_3SO_3^-$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 145.3 (s, 1 C, 2′-C), 143.9 (s, 1 C, 3-C), 138.4 (q, *J* = 1.8 Hz, 1 C, 3′-C), 138.3 (s, 1 C, 4-C), 136.0 (q, *J* = 2.2 Hz, 1 C, 4′-C), 134.6 (q, *J* = 1.1 Hz, 1 C, 5′-C), 134.0 (q, *J* = 1.0 Hz, 1 C, 2-C), 132.4 (s, 1 C, 5-C), 132.0 (s, 1 C, 6′-C), 130.1 (q, *J* = 1.3 Hz, 1 C, 6-C), 128.8 (q, *J* = 309.3 Hz, 1 C, SCF_3), 123.5 (q, *J* = 328.6 Hz, 1 C, S^+CF_3), 120.8 (q, *J* = 320.4 Hz, 1 C, $CF_3SO_3^-$), 119.3 (s, 1 C, 1′-C), 115.4 (s, 1 C, 1-C), 21.5 (s, 1 C, 3-Me), 20.5 (q, *J* = 0.8 Hz, 1 C, 2′-Me) ppm. HRMS: calcd. for $C_{16}H_{13}F_6S_2$ 383.0363; found 383.0343 (δ = –5.2 ppm).

Supporting Information (see footnote on the first page of this article): Copies of ^1H, ^{19}F, and ^{13}C spectra of compounds **5a**–**e** with full data and NMR assignments. Enlarged version of Figure 1.

Acknowledgments

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[17] A sample tube was prepared containing equimolar quantities of independently synthesized relevant fluorinated species [excluding phenyl trifluoromethyl sulfoxide (**1c**)] in triflic anhydride solution with a solution of sodium trifluoromethanesulfinate in D_2O contained in an internal capillary (δ = –88.0 ppm) as reference for comparison with our initial NMR experiment. Compounds involved and chemical shifts were as follow: sulfonium **5a**, –42.9 ppm (SCF_3), –51.0 ppm (S^+CF_3), –79.7 ppm (TfO^-); $PhSCF_3$ **6**, –45.3 ppm; triflic anhydride, –74.1 ppm; triflic acid, –79.7 ppm (exchanging with TfO^-); $PhSO_2CF_3$, –81.0 ppm.

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