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Arylsulfur trifluorides: Improved method of synthesis and use as *in situ* deoxofluorination reagents

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ABSTRACT

Building on recent results of Umemoto and Winter, an improved method of synthesis of arylsulfur trifluorides, including the excellent, new deoxofluorination reagent Fluolead, is hereby reported. The method utilizes Br_2 and KF as oxidizing and fluorinating reagents for efficient, high yield conversion of aryl disulfides and mercaptans to arylsulfur trifluorides. It has also been shown that both Fluolead and mesitylsulfur trifluoride may be generated in acetonitrile and used as *in situ* deoxofluorination reagents for conversion of either aldehydes or ketones to their respective *gem*-difluoro compounds. An analysis of the probable mechanism of action, including computational efforts, allows postulation of a rationale for the highly variable reactivities of different arylsulfur trifluorides as deoxofluorination reagents.

1. Introduction

Selective incorporation of fluorine into organic molecules continues to be an important and ever-challenging component in the design and synthesis of effective pharmaceuticals and agrochemicals [1–4]. Considering the various techniques that are utilized to accomplish such incorporation, deoxofluorination reactions must be considered among the most important. Deoxofluorination reactions include most notably the direct conversion of alcohols to alkyl fluorides, ketones and aldehydes to *gem*-difluoroalkanes and carboxylic acids to trifluoromethyl groups.

The discovery that SF_4 is an effective reagent for carrying out such transformations [5,6] was a key factor in propelling the emerging field of synthetic organofluorine chemistry into the main stream of synthetic organic chemistry during the 1960s. In the ensuing years other reagents, essentially derivatives of SF_4, emerged as safer, more convenient, and sometimes superior deoxofluorination reagents. The best known, and most widely used among them are DAST (diethylaminosulfur trifluoride) [7] and Deoxo-Fluor (bis(2-methoxyethyl)aminosulfur trifluoride) [8], although there are many others that have more limited applicability (Fig. 1)

Recently, two other broadly effective deoxofluorination reagents have been reported, Xtal-Fluor (the E-version being derived from DAST) [9] and Fluolead, a crystalline, thermally stable, highly reactive arylsulfur trifluoride [10–14]. Xtal-Fluor requires a fluoride source such as Et_3N-3HF to generate DAST-like reactivity whereas Fluolead has been found to have broad and highly efficient reactivity with alcohols, aldehydes, ketones and carboxylic acids, as exemplified in Scheme 1 [10,14]. The excellent reactivity of Fluolead contrasts with earlier reports regarding arylsulfur trifluorides, which have been found to be relatively ineffective as deoxofluorination agents [14,15]. Interestingly, all of the above broadly effective, diverse deoxofluorination reagents are fluorosulfur compounds.

According to Umemoto's disclosures, Fluolead can be prepared by treating an acetonitrile solution of precursor disulfide, **1a**, with 3.5 equiv. of chlorine in the presence of 10 equiv. of anhydrous KF. The Cl_2 was slowly bubbled into the ice-bath-cooled solution over a period of 2 h. After filtration and distillation, a yield of 68% of Fluolead could be obtained (Scheme 2) [14].

The toxicity of gaseous Cl_2 and control of its addition to the reaction mixture can pose practical problems in the laboratory synthesis of Fluolead. Moreover, when working with aryl disulfides other than **1a**, if the amount of Cl_2 is not carefully controlled and the reaction not carefully monitored, there is the possibility of partial over-chlorination of the arylsulfur trifluorides to form chlorotetrafluorosulfanyl compounds, such as **3** in Scheme 3. Umemoto has demonstrated that such exhaustive chlorination of arylsulfur trifluorides to form the aryl chlorotetrafluorosulfanyl compounds can be put to good use, since intermediates such as **3** can be readily converted to the analogous aryl-SF_5 compounds (Scheme 3) [16,17].

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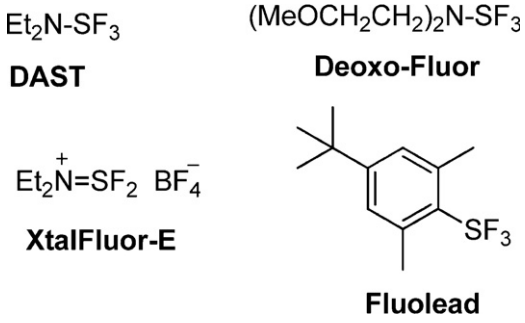


Fig. 1. Major deoxofluorination reagents.

Recently Winter and Cook reported an efficient new method for preparation of SF_4, converting elemental sulfur to SF_4 through treatment with Br_2 and KF (Eq. (1)) [18].

$$S + 2Br_2 + 4KF \rightarrow SF_4 \quad (1)$$

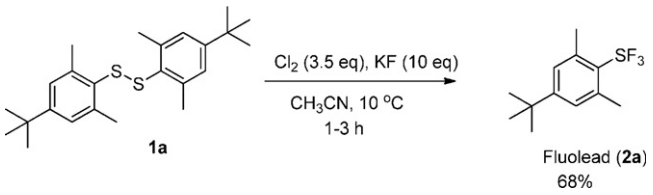
Bromine is easier to handle and quantities are more readily controlled than is the case for chlorine. Because of our past interest in organic SF_5 compounds [19,20], we considered the possibility of applying the Winter/Cook chemistry to Umemoto's approach to aryl-SF_5 compounds in the hope of enhancing his procedure. In our hands the aryl-SF_4Cl compounds, such as **3**, were unstable and difficult to handle and convert to the respective Ar-SF_5 compounds, and we thought that the respective bromides might provide some advantage.

2. Results and discussion

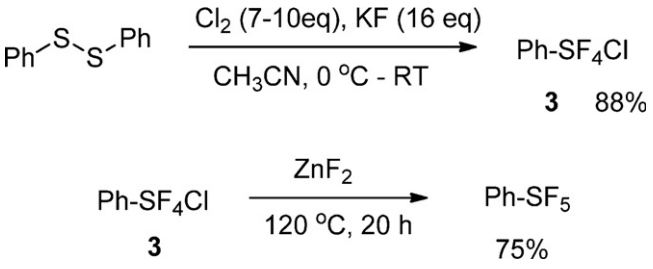
2.1. Improved synthesis of arylsulfur trifluorides

What was in fact observed was that when phenyl disulfide (**1b**) was allowed to react with excess Br_2 and dry, excess KF in acetonitrile, the reaction came to a *complete stop* with formation of Ph-SF_3 (Scheme 4). A ^{19}F NMR spectrum of the reaction mixture taken after 2 h at 0 °C (Fig. 2) indicates how clean this reaction is. Only a small amount of phenyl sulfinyl fluoride (**4**), deriving from not quite dry KF, contaminates the product mixture. This result was disappointing with respect to possible use of these conditions to prepare aryl-SF_5 compounds, but it provided a distinct advantage for the synthesis of aryl-SF_3 compounds when compared to the chlorine-induced procedure of Umemoto. Indeed, when this procedure was used to prepare. Fluolead, a 65% yield was observed after 2 h at 0 °C, with 85% of Fluolead being obtained upon stirring at room temperature for 4 additional hours. Further study indicated that three equivalents of Br_2 and six of KF were sufficient to convert all of an aryl disulfide to the arylsulfur trifluoride.

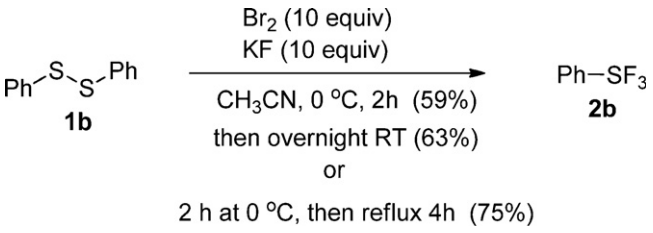
Aryl thiols could also be converted to their respective arylsulfur trifluorides under similar conditions, as is exemplified for the reaction of benzene thiol (Scheme 5).



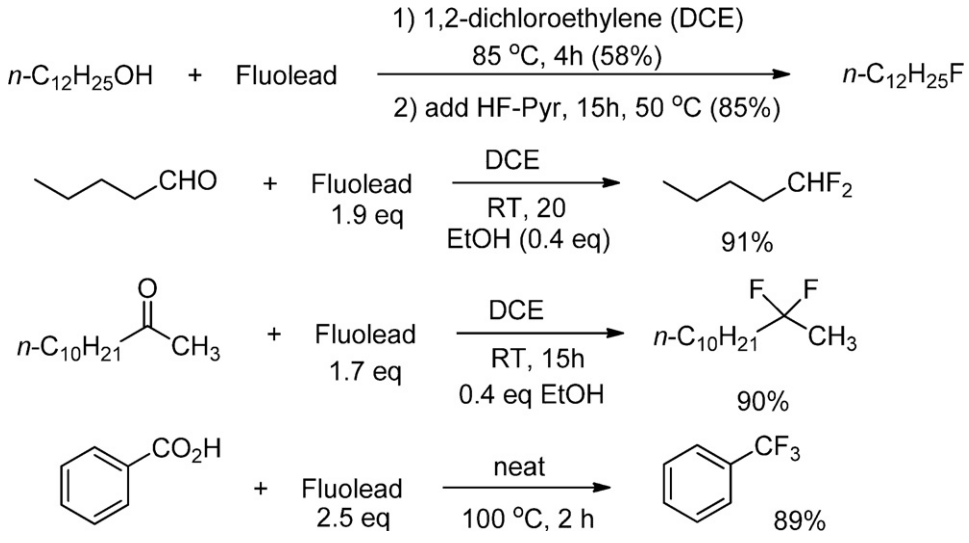
Scheme 2. Umemoto synthesis of Fluolead.



Scheme 3. Example of the Umemoto process for synthesis of aryl-SF_5 compounds.



Scheme 4. Initial experiments replacing chlorine with bromine.



Scheme 1. Typical Fluolead deoxyfluorinations.

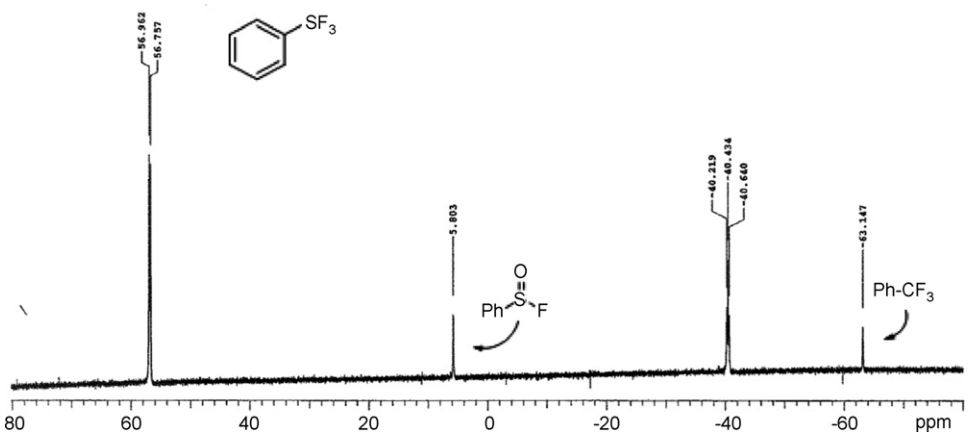
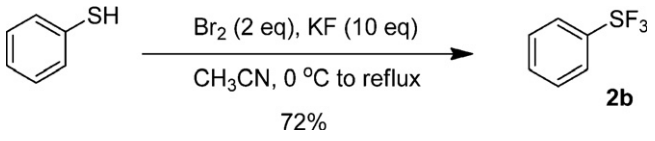


Fig. 2. ^{19}F NMR spectrum of the reaction mixture after 2 h at 0 °C.

Although Fluolead is an outstanding deoxofluorination reagent, with broad applicability, there are problems associated with its preparation, storage and use. Fluolead, like all other arylsulfur trifluorides, is corrosive to glass and moisture sensitive. The major impurity in samples of Fluolead is the respective arylsulfinyl fluoride compound (**4**). Sulfinyl fluoride **4** is derived from the reaction of the Fluolead SF_3 group with traces of water in the reaction mixture, and its formation is very difficult to avoid. With that in mind, effort must be made to use the driest possible KF in the preparation of Fluolead. This sulfinyl fluoride is also the co-product from Fluolead in its deoxofluorination reactions (Scheme 6), and it is itself corrosive to glass.

The corrosive natures of arylsulfur trifluorides and arylsulfinyl fluorides do not appear to simply derive from HF that might be generated from them. As noted by Sheppard in his early preparation of phenylsulfur trifluoride [21,22], both of them appear, even when pure, to slowly react with glass. Thus Fluolead must be stored in flasks made of fluoropolymer, and reactions of Fluolead are best carried out in fluoropolymer bottles or flasks.

Nevertheless, in spite of the above practical challenges, the ease of synthesis of Fluolead, combined with its potential low cost and its excellent reactivity characteristics with respect to its deoxofluorination reactions might well make it the reagent of choice for carrying out such transformations.



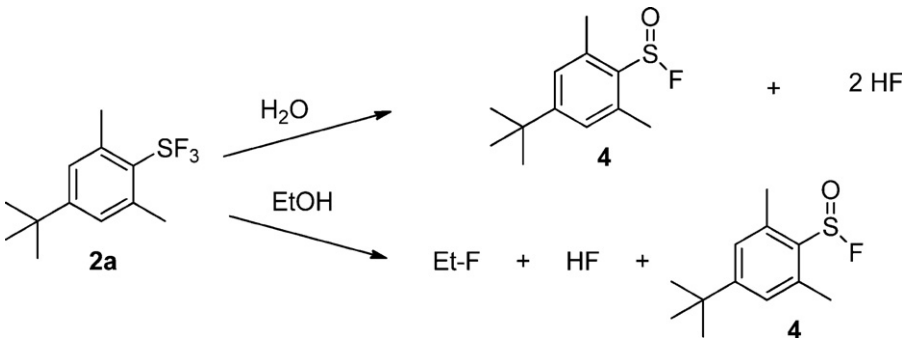
Scheme 5. Use of benzene thiol in preparation of phenylsulfur trifluoride.

2.2. In situ use of Fluolead

It was hypothesized that those problems associated with the preparation and use of Fluolead might well be minimized or alleviated by its generation and use *in situ*. In addition, scrupulously dry KF would not be required, since one could simply use a slight excess of reactants in order to compensate for partial loss of Fluolead due to hydrolysis.

Indeed, it was found that the acetonitrile reaction mixture containing prepared Fluolead *can* be used directly to carry out its reactions with aldehydes and ketones. In the initial experiments, 10 equiv. of Br_2 and dry KF were used per equivalent of disulfide. After addition of Br_2 at 0 °C was complete, the reaction was warmed to RT and stirred for 2 h, at which time full conversion to Fluolead was observed by fluorine NMR. Benzaldehyde (0.75 equiv.) was then added and the mixture allowed to stir at room temperature with no significant amount of product being observed after 24 h. Umemoto had shown that the reaction of Fluolead with aldehydes is complete at room temperature after 20 h when the reaction is carried out in 1,2-dichloroethane (DCE) (Scheme 1) [14]. Thus the mixture of *in situ*-generated Fluolead in acetonitrile is less reactive than that of pure Fluolead in DCE. However, when the reaction mixture was then heated at reflux for 16 h, a very good (72%) yield of difluoromethylbenzene was obtained.

Later, after some optimization of the *in situ* Fluolead reactions, the minimum amounts of Br_2 and KF (3 equiv. and 6 equiv., respectively) were found to be sufficient for reaction with disulfide **1a** in acetonitrile at RT for 2 h, after which about 0.75 equiv. of aldehyde or ketone were added and the mixture heated to reflux for 16 h. Examination of the reaction mixtures by fluorine NMR at that time indicated complete conversion of the respective



Scheme 6. Formation of sulfinyl fluoride coproduct from Fluolead.

Table 1
In situ generation and use of Fluolead.

Reactant	Product	Yield (%)
Benzaldehyde	$PhCHF_2$	72[a]
p-Bromobenzaldehyde	*p*-$BrPhCHF_2$	80[a]
p-Tolualdehyde	*p*-$MePhCHF_2$	76[a]
Acetophenone	$PhCF_2CH_3$	70[b]
2-Butanone	$CH_3CH_2CF_2CH_3$	45[b]
Isobutyraldehyde	$(CH_3)_2CHCF_2H$	49[b]

[a] Isolated yield.
[b] NMR yield.

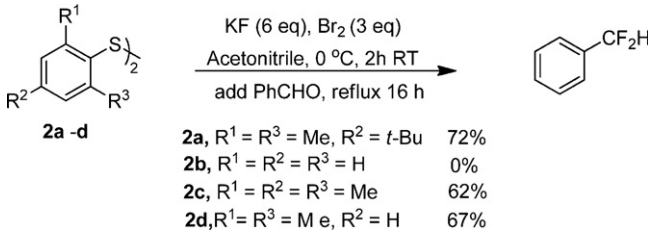
substrates with the (unoptimized) yields of products indicated in Table 1. Products were isolated after extraction by hexane and hydrolysis of the sulfinyl fluoride co-product by treatment with 10% aq. NaOH.

Unfortunately, it was found that conversion of alcohols to fluorides under the above-described *in situ* conditions was not possible. No fluorinated products were able to be observed when primary alcohols were used as substrates under the conditions given in Scheme 7. The lack of fluoride product has been demonstrated to derive from interception of the initially formed intermediate (**5**) by bromide ion, in competition with fluoride ion (Scheme 8). Bromide ion is much more nucleophilic than fluoride ion, and it should also be present in much greater concentration than fluoride ion. An interesting, still unanswered question remains as to why bromide did not compete with fluoride during the *in situ* reactions of ketones and aldehydes. In those reactions, no significant amounts of bromofluoro products were observed by fluorine NMR.

2.2.1. Alternative arylsulfur trifluorides

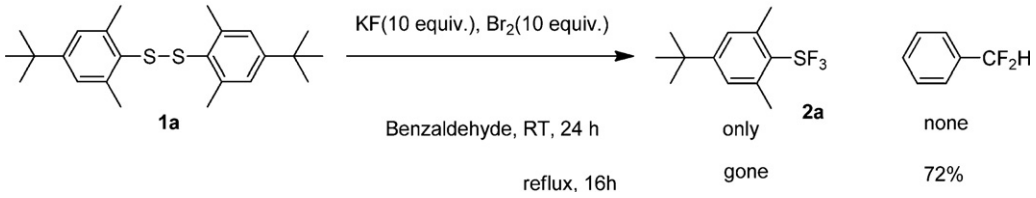
In addition to its high reactivity and thermal stability, Fluolead has a number of other attributes which make it convenient and safe to use. It is a crystalline solid, easy to handle, does not fume and it reacts with water only slowly. These latter properties become less important if one chooses to use the reagent *in situ*. Thus, if simpler arylsulfur trifluorides were to exhibit similar *in situ* reactivity, the lower cost of such reagents might then make them preferred over Fluolead for an *in situ* process. Phenyl and mesityl disulfides are readily available, either commercially or from reduction of the respective sulfonylchlorides [23], and our Br_2/KF process proved successful for conversion of each to its respective $ArSF_3$ reagent (>70% yields for each).

When these reagents were used as *in situ* deoxofluorination reagents, it was found that $PhSF_3$ was ineffective as an *in situ* reagent in acetonitrile, giving no observable difluoromethylbenzene product after 24 h of reflux with benzaldehyde. This is consistent with Umemoto's finding that $PhSF_3$ is considerably less effective than Fluolead in its reactions in DCE [14]. The interesting thing about the current results, however, is that $PhSF_3$, under our *in situ* reaction conditions in acetonitrile, appears to be essentially *untouched* by the added benzaldehyde reactant. A fluorine NMR spectrum of the reaction mixture shows the $PhSF_3$ present and unreacted. On the other hand, the mesityl reagent (2,4,6-trimethylphenylsulfur trifluoride) exhibited reactivity with benzaldehyde that was very similar to that of Fluolead, giving an unoptimized 62% yield of difluoromethylbenzene from benzaldehyde (Scheme 9).

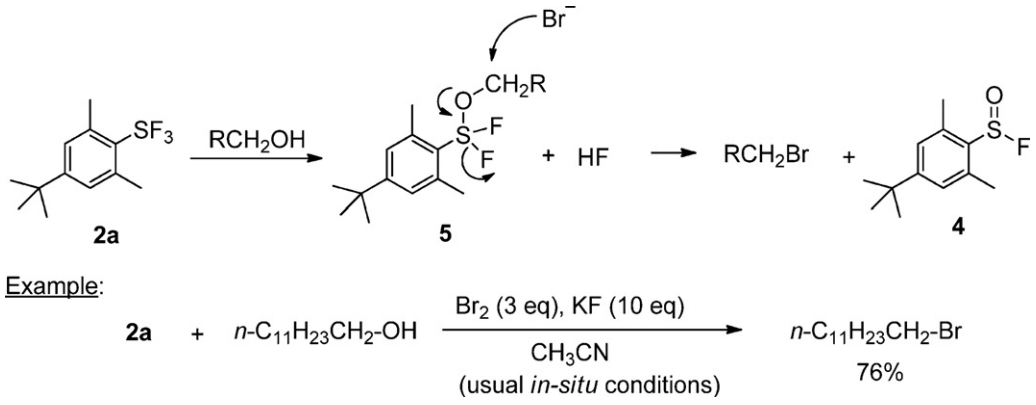


Scheme 9. *In situ* reactions of various arylsulfur trifluorides.

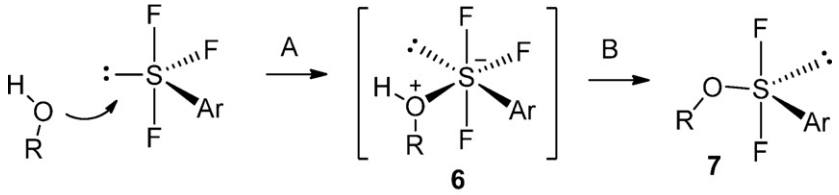
Scheme 7. First attempt at *in situ* reaction with Fluolead



Scheme 7. First attempt at *in situ* reaction with Fluolead.

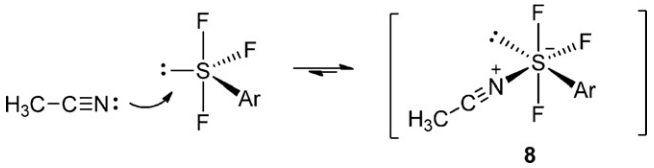


Scheme 8. Reaction of alcohols with Fluolead under *in situ* conditions.



Scheme 10. First step of the mechanism of nucleophilic attack on Ar-SF_3.

On the basis of these results, and those reported by Umemoto, we concluded that the two *ortho* methyl substituents of Fluolead were probably critical to allowing it to react in acetonitrile, which implied that its *p*-*t*-butyl group should not necessarily be required from a reactivity point of view. This hypothesis was further tested by synthesizing 2,6-dimethylphenyl disulfide and examining its *in situ* reactivity with benzaldehyde, which in the event was similar to that of the mesityl system (Scheme 9).



Scheme 11. Interaction of nucleophilic solvent with $ArSF_3$.

2.3. Mechanistic considerations

All Ar-SF_3 compounds exist as trigonal bipyramids with fluorines always preferring the axial position and with the lone pair in the equatorial position along with the aryl group. As exemplified for the initial stages of the reaction of an alcohol with Ar-SF_3 (Scheme 10), in undergoing reaction its trigonal bipyramid SF_3 group is converted initially (Step A) to an octahedral complex **6**, which then eliminates HF (in Step B) to regenerate a trigonal bipyramid species, intermediate **7** [24].

The mechanism of Scheme 10 should be able to allow us to rationalize two reactivity issues. First, why are the *ortho*-disubstituted $ArSF_3$ reagents (i.e., Fluolead) more effective than $PhSF_3$ as deoxofluorination reagents? Both should be reactive with respect to nucleophilic attack, but only Fluolead gives high yields of fluorinated products. We believe that this disparity in effectiveness can indeed be explained by Scheme 10. A reasonable rationale is that although both $PhSF_3$ and Fluolead participate in the first step (A) (Fluolead probably slower than $PhSF_3$), the sterically-more-demanding Fluolead complex executes the second step (B) much faster than $PhSF_3$. The octahedral complex (**6**) is a more crowded environment than either $ArSF_3$ or the following intermediate **7**, and therefore the *ortho* substituents on Fluolead should destabilize this intermediate and accelerate its conversion to **7**, thus moving the overall deoxofluorination process forward.

The second issue that requires explanation is why the *in situ* process, in acetonitrile, proceeds efficiently (albeit more slowly than in DCE) when using the sterically hindered Fluolead, but no reaction at all occurs when using $PhSF_3$. It is proposed that both the *lack* of reaction of $PhSF_3$ and the *diminished reactivity* of Fluolead derive from the variable extent of reversible, non-productive complexation that they undergo with a nucleophilic solvent such as acetonitrile (Scheme 11).

Based upon calculations discussed below, it is contended that the equilibrium interaction of the solvent acetonitrile with $PhSF_3$ depicted in Scheme 11 favors complex **8** to such an extent that nucleophilic attack by the more nucleophilic alcohol and carbonyl substrates is essentially *kinetically* prohibited. This conclusion is supported by the experimental observation mentioned earlier that

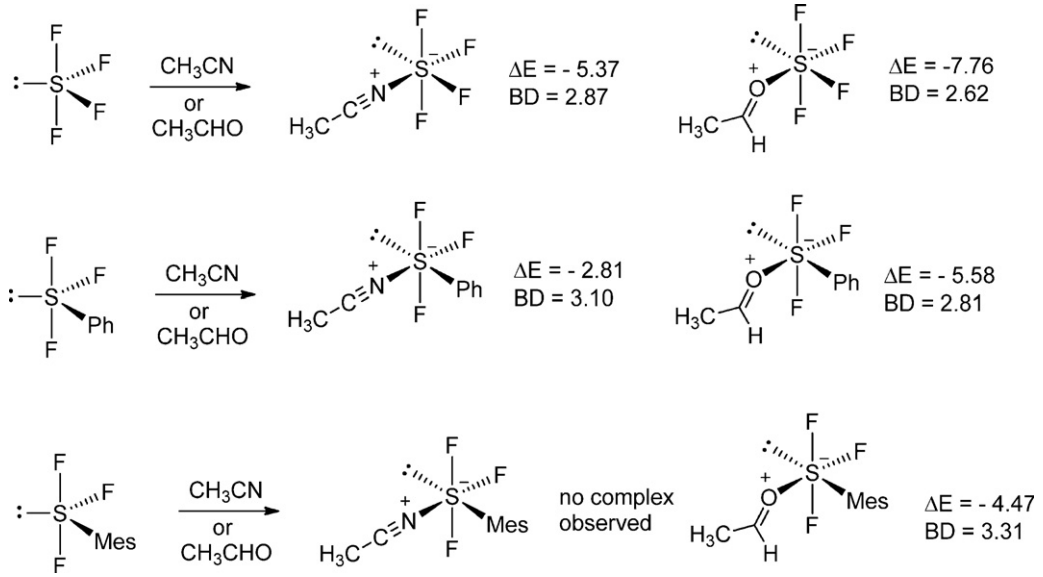


Fig. 3. Energies (kcal/mol) and N–S or O–S bond distances (angstroms, Å) of complexes with acetonitrile and acetaldehyde.

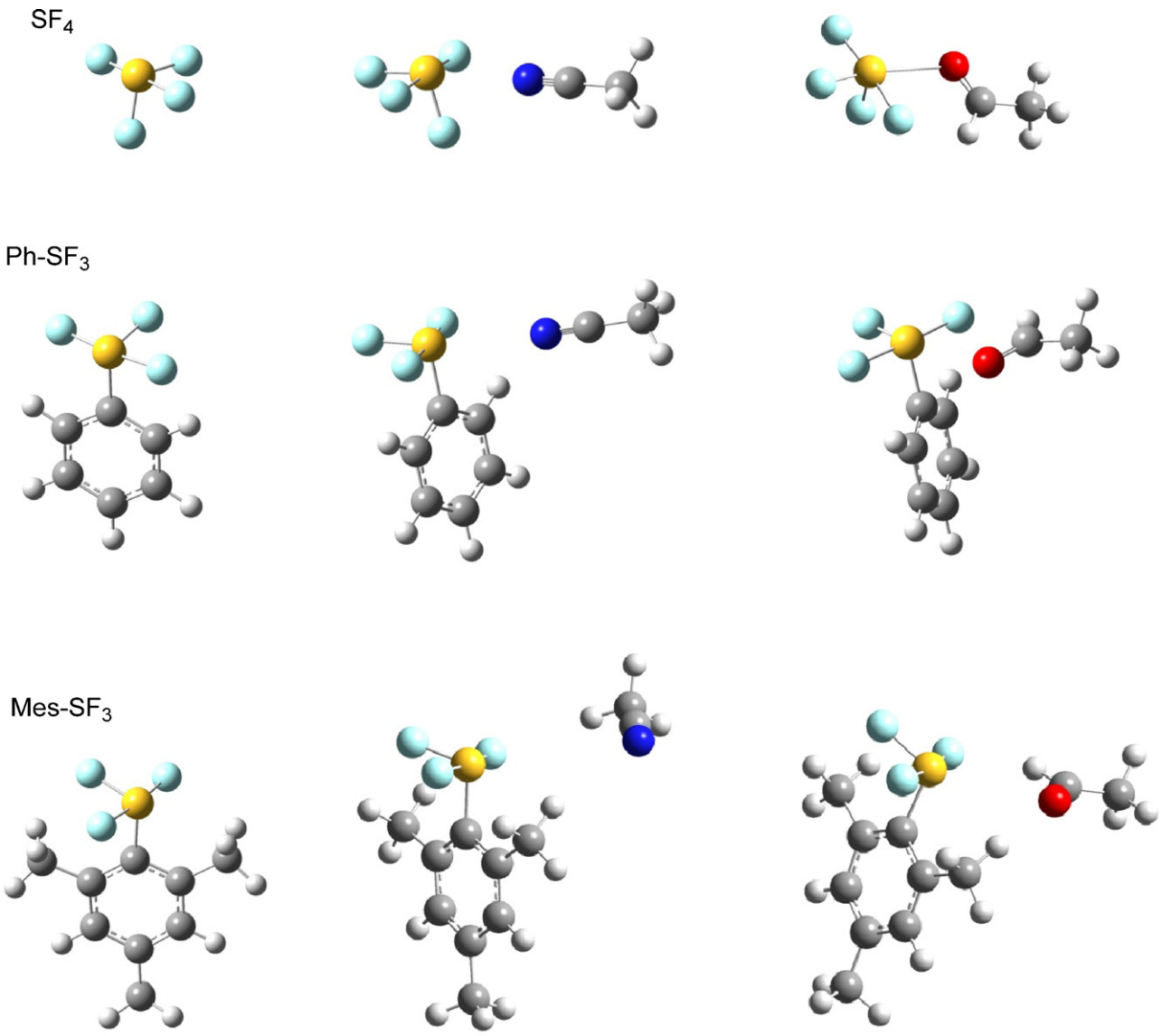


Fig. 4. Computed structures of complexes with acetonitrile and acetaldehyde.

$PhSF_3$ remains unreacted and untouched by added benzaldehyde when used under *in situ* conditions.

2.4. Computational results and discussion

In order to provide additional evidence for these mechanistic proposals, the structures of SF_4, $PhSF_3$ and mesityl-SF_3 and the structures and relative energies of their complexes with acetonitrile and acetaldehyde were examined computationally in the gas phase at B3LYP/6-311G(d,p) levels of theory using the Gaussian 03 Rev. E01 package [25] (Fig. 3). Depictions of the computed structures for the various species and their complexes are provided in Fig. 4.

The calculations of ΔE are consistent with acetonitrile binding strongly to SF_4 and somewhat strongly to Ph-SF_3, while not binding significantly to mesityl-SF_3. The more nucleophilic acetaldehyde binds much more strongly to both SF_4 and Ph-SF_3, and even shows significant binding to mesityl-SF_3. Comparing the combined van der Waals radii for S–N and S–O (3.35 and 3.33 Å, respectively) with the calculated bond distances for the various complexes provides corroborating evidence of the relative binding within these complexes.

These calculations are consistent with our conclusion that solvent (acetonitrile) binding to the SF_3 group of Ph-SF_3 is sufficiently strong to prevent attack by a reactive nucleophile, whereas Fluolead, having little if any interaction with solvent, remains reactive, although with diminished reactivity.

3. Conclusions

Building on the results of Umemoto and Winter, an improved method of synthesis of arylsulfur trifluorides, including the excellent, new deoxofluorination reagent Fluolead, has been reported. The method utilizes Br_2 and KF as oxidizing and fluorinating reagents for efficient, high yield conversion of aryl disulfides to arylsulfur trifluorides. It has also been shown that both Fluolead and mesitylsulfur trifluoride may be generated in acetonitrile and used as *in situ* deoxofluorination reagents for conversion of either aldehydes or ketones to their respective *gem*-difluoro compounds. An analysis of the probable mechanism of action, including computational efforts, has allowed postulation of a rationale for the highly variable reactivities of different arylsulfur trifluorides as deoxofluorination reagents in acetonitrile. Further details related to the specific relative efficiencies of various aryl

sulfurtrifluorides as deoxofluorination reagents under *in situ* conditions in solvents of variable nucleophilicities will be addressed in future work.

4. Experimental

4.1. Preparation of aryl disulfides [26]

2,6-Dimethylphenyl disulfide (**2d**) was prepared in 40% yield from 2-bromo-1,3-dimethylbenzene via its Grignard reagent, by the method of Davis [27].

Mesityl disulfide (**2c**) was prepared in 70% yield via the sulfonyl chloride [28], using the method of Umemoto [10,14].

4.2. Preparation of phenylsulfur trifluoride from phenyl disulfide

Into a flame-dried 500 mL three-necked flask equipped with a reflux condenser and a dropping funnel was placed anhydrous acetonitrile (120 mL) under nitrogen. Spray-dried potassium fluoride (23.2 g, 400 mmol) was added with stirring, followed by addition of phenyl disulfide (8.72 g, 40 mmol). The mixture was cooled to 0 °C by an ice bath, and bromine (20 mL, 400 mmol) was added dropwise. After addition, the mixture was stirred at 0 °C for 2 h and then warmed to room temperature slowly. Finally, the mixture was heated to reflux and stirred for 4 h. The reaction mixture was cooled to room temperature, and the solvent and excess of bromine were removed under reduced pressure. Hexane (200 mL) was added to the residue and stirred vigorously. The mixture was filtered, the solid washed with hexane, and the solvent removed. Then the residue was distilled under reduced pressure to give a colorless liquid (65 °C/10 mm Hg) (10.0 g, 75% yield) [15]: ^{19}F NMR (CH_3CN) δ −40.46 (t, J = 58 Hz, 1F), +56.81 (d, J = 58 Hz, 2F); impurity of PhSOF at δ +5.76.

4.3. Preparation of phenylsulfur trifluoride from thiophenol

The procedure for the synthesis of phenylsulfur trifluoride from thiophenol is identical to that above for conversion from the disulfide, except that only two equivalents of Br_2 were required for each equivalent of thiophenol. A yield of 72% of phenylsulfur trifluoride was obtained.

4.4. Preparation of 2,6-dimethyl-4-t-butylphenylsulfur trifluoride (Fluolead)

Into a flame-dried 500 mL round-bottomed flask equipped with a dropping funnel was placed anhydrous acetonitrile (120 mL) under nitrogen. Spray-dried potassium fluoride (29.1 g, 500 mmol) was added with stirring, followed by addition of bis(2,6-dimethyl-4-*t*-butylphenyl)disulfide (19.4 g, 50 mmol). The mixture was cooled to 0 °C by an ice bath, and bromine (26 mL, 500 mmol) was added dropwise. After addition, the mixture was stirred at 0 °C for 2 h. The solvent and excess of bromine were removed under reduced pressure at room temperature. After that, the product was distilled under reduced pressure (178 °C/10 mm Hg) to give 17.5 g of a pale white solid (70% yield): ^{19}F NMR (CH_3CN-d_3): δ 50.9 (t, J = 62.7 Hz, 2F), −58.4 (d, J = 62.7 Hz, 1F) [14].

4.5. Typical in situ deoxofluorination procedure

All glassware was flame dried and cooled under nitrogen. The potassium fluoride was dried either by heating at 140 °C under vacuum for 2 h, or by melting in a crucible, followed by grinding to a powder under N_2. Into a 250 mL three-necked flask was charged with potassium fluoride (8.71 g, 150 mmol), disulfide **1a** (9.67 g, 25 mmol) and anhydrous acetonitrile (50 mL) under nitrogen. The mixture was cooled to 0 °C, and then bromine (12 g, 75 mmol) was added dropwise over a period of 15 min. After addition, the cold bath was removed and the reaction was stirred at room temperature for 2 h, after which aldehyde (0.75 equiv. relative to disulfide) was added in one portion. The mixture was heated to reflux and stirred for 16 h, and then cooled to room temperature. Then hexane (100 mL) was added, followed by 50 mL of water, and the upper layer was separated and washed with brine. The hexane extract was then stirred with 10% sodium hydroxide (50 mL) for 1 h. The upper layer was isolated and dried over sodium sulfate, and then the product was purified by column chromatography or by distillation.

Acknowledgments

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