Synthetic Methods

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Synthesis and Characterization of 2-Pyridylsulfur Pentafluorides**

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Abstract: *Current approaches to prepare SF_5-substituted heterocycles during the synthesis of targeted heterocyclic compounds require the use of SF_5-functionalized aryl or alkyne reagents or SF_5Cl as a source of the SF_5 functional group. Herein we report that excess oxidative fluorination of 2,2′-dipyridyl disulfide with a KF/Cl_2/MeCN system leads to the formation of thirteen new 2-pyridylsulfur chlorotetrafluorides (2-SF_4Cl-pyridines). These molecules are found to undergo further chlorine–fluorine exchange reactions by treatment with silver(I) fluoride enabling ready access to a series of ten new substituted 2-pyridylsulfur pentafluorides (2-SF_5-pyridines). This is the first preparatively simple and readily scalable example of the transformation of an existing heterocyclic sulfur functionality to prepare SF_5-substituted heterocycles.*

The pentafluorosulfanyl (SF_5) group has unique physicochemical properties that have great potential for the development of new materials, pharmaceuticals, and agrochemicals. Several reviews highlighting aspects of the chemistry of the SF_5 group, including its intriguing properties, have been published.[1] Over the last few years, the number of patents and research papers dealing with molecules that contain the SF_5 substituent has increased rapidly. This upsurge of interest has been facilitated to a significant extent by the increased commercial availability of simple aromatic SF_5 building blocks, which became possible as a result of new method developed by Umemoto et al.[2] Implementation of Umemoto's procedure has allowed the commercial preparation of a large diversity of SF_5-substituted aryl compounds.[2] The SF_5 substituent is now considered a potentially superior replacement for the CF_3 group in terms of lipophilicity, chemical stability, electronegativity, and steric bulk—critical parameters in discovering new or improving methods for the preparation of established bioactive molecules. Several recent examples have confirmed the fact that exchanging the CF_3 group to a SF_5 group in molecules with biological activity can greatly enhance their potency and/or selectivity.[3] Therefore, the development of synthetic methods for producing novel SF_5-containing molecules and building blocks remains a research area of great current activity, with particular needs in the area of SF_5-substituted heterocycles.

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A search on reported SF_5-substituted heteroaryl compounds reveals 23 citations (16 papers and 7 patents).[4] Analysis of these citations enables the division of reported SF_5-substituted heteroaryls into two major groups. The first group is larger and is composed of fused bicyclic heterocycles, where the SF_5 group is attached to the benzene part of a benzannulated heterocycle. These compounds have always been prepared from a SF_5-substituted aryl precursor, exploiting well-known cyclization techniques to build heterocyclic systems of indole,[5a,b] indazole,[5c] benzimidazole,[5d–f] benzoxazole,[5g] benzisoxazole,[5h] benzothiophene,[5a] benzothiazole,[5i] benzotriazole,[5d] quinoline,[3d,e,h,5h] quinoxaline,[5d] and quinazoline.[5h] The second smaller group comprises monocyclic aromatic SF_5-substituted heterocycles: pyrroles,[5j,k] furans,[5l,m] thiophenes,[5j,k] pyrazoles,[5n,o] isoxazoles,[5m] and triazoles.[5o–q] Routes to those heterocycles utilized either 1,3-dipolar cycloaddition reactions with SF_5-substituted alkynes or retro-Diels–Alder reactions of bridged SF_5-containing precursors. One unique example describes the preparation of SF_5-thienylthiophene by intramolecular addition/cyclization of lithium thiolate to an SF_5-substituted alkyne fragment.[5r] Many of these SF_5-containing heteroaryl molecules were claimed to exhibit various types of biological activity.

The pyridine ring is among one of the most common and well-recognized structural components of alkaloids as well as hundreds of currently developed or already marketed drugs and agrochemicals,[6] some of them containing the pyridine unit bearing an α-CF_3 substituent (Figure 1). However, only two reports are related to the preparation of SF_5-substituted pyridines. The synthesis of 4-SF_5-2,3,5,6-tetrachloropyridine was briefly reported in 30–40% yield by heating the corresponding thiol with IF_5 but no experimental or characterization details were provided.[7a] The second report is a patent describing the synthesis of 2-SF_5-pyridine by oxidative fluorination of 2,2′-dipyridyl disulfide with the strong oxidizing fluorinating reagent AgF_2 in nonane for 5 hours at 120 °C.[7b] Drawbacks of this preparation, as mentioned in the patent, are: the use of special reaction equipment (copper reactor with a polytetrafluoroethylene (PTFE) closure and a copper condenser), the required excess of AgF_2 (14–18 equivalents per mole of disulfide), and finally the low purity of the isolated 2-SF_5-pyridine, which was estimated by GC as 70% (Scheme 1). No additional examples or further development of either method have been reported. Also, the two pyridine examples are the only reports on the conversion of an existing heterocyclic sulfur functionality into an SF_5 group. Additionally, examples of heterocycles with an SF_5 group in the α position to a heteroatom are limited to pyrazoles,[5n,o] triazoles,[5o–q] and pyridine.[7b]

The synthesis of arylsulfur pentafluorides by Umemoto's procedure requires two key steps.[2] The first step is the

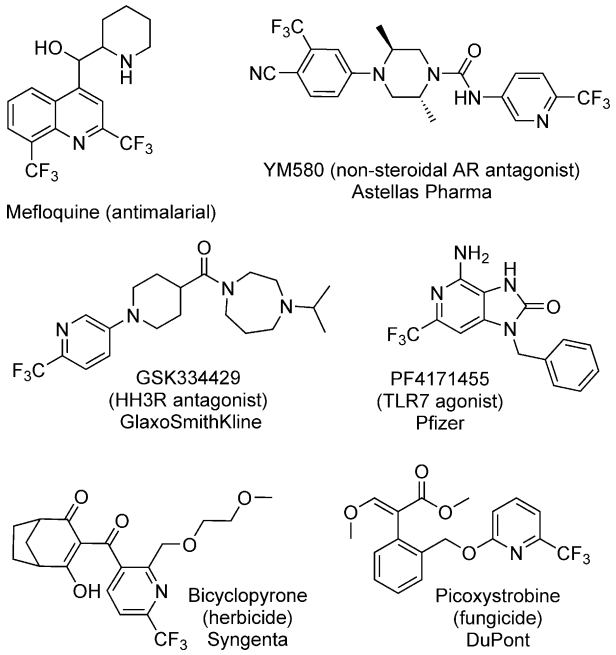
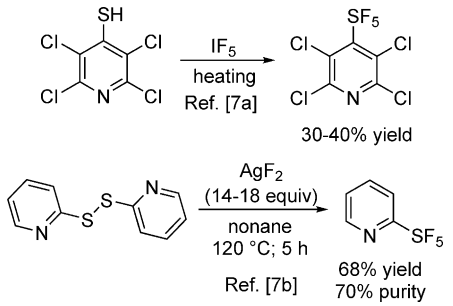


Figure 1. Bioactive compounds with an α-CF_3-pyridine fragment. AR = androgen receptor. HH3R = histamine H(3) receptor. TLR7 = toll-like receptor-7.



Scheme 1. The two reported synthetic routes for SF_5-substituted pyridines.

preparation of arylsulfur chlorotetrafluoride ($ArSF_4Cl$) intermediates starting from a corresponding aromatic thiol, disulfide, or sulfenylchloride, utilizing the extended reaction conditions (KF/Cl_2/MeCN) of Shermolovich and co-workers.[8a] These conditions were originally reported for the oxidative fluorination of R-S-S-R sulfur derivatives to access organosulfur trifluorides ($R\text{-}SF_3$).[8a] The second step involves chlorine–fluorine exchange of the SF_4Cl group to obtain the target SF_5-substituted aryl products. This step is generally carried out using anhydrous HF or its complexes or by treatment with one of a wide range of inorganic fluorides. There are no reports of utilizing the Umemoto method to synthesize SF_4Cl- or SF_5-substituted heterocycles, although two papers from Shermolovich et al. described the preparation of SF_3-benzothiazole,[8a] and 2-pyridyl, 1-oxo-2-pyridyl, and 2-pyrimidinylsulfur trifluorides[8b] using the KF/Cl_2/MeCN conditions. As arylsulfur trifluorides have been shown to be intermediates during the formation of SF_4Cl-substituted aryl compounds,[2] it was logical to investigate the same route to prepare pyridyl-SF_4Cl compounds as precursors to the corresponding SF_5-substituted pyridines.

In this Communication, we report our work on the application of the method of Umemoto and co-workers to pyridines, which has resulted in the preparation of the first series of 2-SF_5-pyridine derivatives.

2,2′-dipyridyl disulfide, a readily available and relatively inexpensive compound, was used as the starting material in our initial studies. Applying conditions analogous to those used for the reaction of diphenyl disulfide, that is, 16 equivalents of KF and 8 equivalents of Cl_2 per 1 equivalent of disulfide in acetonitrile,[2] and monitoring the reaction course by ^{19}F NMR spectroscopy, enabled us to detect the formation of 2-pyridylsulfur chlorotetrafluoride (**2a**) as the sole product after 16 hours at ambient temperature. A signal at $\delta = +125$ ppm in the ^{19}F NMR spectrum of **2a** confirms exclusive formation of the *trans* isomer.[9] 2-Pyridylsulfur chlorotetrafluoride (**2a**) was isolated after filtration and solvent evaporation as a viscous liquid which is extremely sensitive to moisture, fuming when exposed to air, and vigorously reacting with water. It also reacts with glass particularly rapidly at elevated temperatures. Reactions with water or glass produce pyridine-2-sulfonyl chloride and HF or SiF_4, respectively. On the basis of its ^1H, ^{19}F, and ^{13}C NMR spectra, the purity of **2a** could be estimated at 90–95%. It was noticed that to achieve the highest possible purity of crude 2-SF_4Cl-pyridine and to diminish byproduct formation, a fluoropolymer reaction vessel should be used in its preparation, and the disulfide, KF, and MeCN reagents employed in the reaction should be as dry as possible.

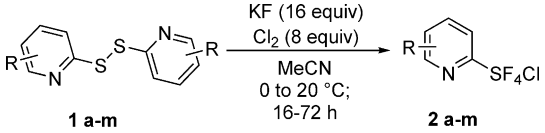
It was clear from the studies of Umemoto et al. that the halogen-exchange reactions with electron-deficient SF_4Cl-substituted aryl compounds were difficult, requiring harsher conditions and proceeding with lower yields.[2] Thus, *p*-NO_2-phenyl-SF_4Cl required reaction with ZnF_2 for 12 hours at 150 °C to produce *p*-NO_2-phenyl-SF_5 in only 36% yield. Effective chlorine–fluorine exchange reactions with aromatic polyfluoro-, bis-, and tris-sulfur chlorotetrafluorides could be achieved only with very strong fluorinating agents, such as SbF_5.[2]

The unique character of signals for the SF_5 group in ^{19}F NMR spectra allowed rapid screening of fluorination reaction effectiveness on 2-pyridyl-SF_4Cl substrate **2a**, which also confirmed the complexity of that transformation. Many widely used fluorinating reagents were tested in the reaction, with decomposition of the starting material being the typical result. Two of the most powerful available fluorinating reagents, SbF_3 and SbF_5, which usually worked well on deactivated aromatic compounds, gave only trace amounts of the desired 2-SF_5-pyridine derivative. However it was noticed that when silver salts, such as $AgBF_4$, $AgSbF_6$, and AgF, were used in the fluorination step, resonance signals attributable to small amounts of 2-SF_5-pyridine were consistently detected in ^{19}F NMR spectra of the reaction mixtures. Finally, it was found that performing the reaction with AgF, a very effective reagent for halogen-exchange reactions, gave the best result when it was carried out in a closed PFA (perfluoroalkoxy) vial at 60 °C without solvent, and the desired 2-SF_5-pyridine (**3a**)

could be obtained and isolated in 45% yield. If the same reaction was run in a glass vessel, total decomposition of the starting material to pyridine-2-sulfonyl chloride occurred, which then reacted with AgF to produce pyridine-2-sulfonyl fluoride ($\delta_F = +55$ ppm). The two-step reaction starting from disulfide **1a** (11 g; 0.05 mol) was then successfully scaled up giving intermediate **2a** in 95% yield (21 g) and 52% yield of 2-SF_5-pyridine (**3a**; 9.5 g) as a colorless volatile liquid with a camphoraceous odor. In its ^{19}F NMR spectrum, the two signals attributable to the SF_5 group of **3a** appear at $\delta = +51.6$ ppm (d, 4F, $J = 149.6$ Hz) and $+77.9$ ppm (m, 1F).

After developing suitable conditions for the two-step transformation of 2,2′-dipyridyl disulfide (**1a**) into 2-SF_5-pyridine **3a**, exploration of the scope and possible limitations of this route with regard to preparation of substituted 2-SF_5-pyridines was initiated. The work of Umemoto et al.[2] provided insight regarding aryl ring substituents that were compatible with the oxidative fluorination reaction conditions in that work. Such substituents included Me, *t*Bu, CF_3, CCl_3, F, Cl, Br, and NO_2. Commercial availability of simple ring-substituted 2,2′-dipyridyl disulfides or thiols turns out to be quite limited, with compounds being high priced, when available. Therefore, it was generally necessary to synthesize the required eleven disulfides **1b**–**l** (see the Supporting Information).

Disulfides **1c**, **d**, **f**, **g**, and **h** were found to readily form the respective 2-pyridylsulfur chlorotetrafluorides (Scheme 2).

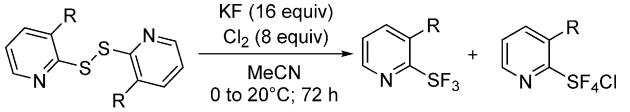


a) R = H; **b**) R = 3-Me; **c**) R = 4-Me; **d**) R = 5-Me; **e**) R = 6-Me (**2e**: 2 products- R = 5-Cl and 6-Me); **f**) R = 5-F; **g**) R = 5-Cl; **h**) R = 5-Br; **i**) R = 3-F; **j**) R = 3-Cl; **k**) R = 3-Br; **l**) R = 5-CF_3; **m**) R = 5-NO_2

Scheme 2. Synthesis of 2-pyridylsulfur chlorotetrafluorides **2a**–**m**.

Aberrant behavior was detected for 6-methyl-substituted disulfide **1e**, which in addition to 2-pyridylsulfur chlorotetrafluoride formation underwent ring chlorination at the 5-position. Also, the reactivities of all 3-substituted disulfides, **1b**, **i**, **j**, and **k** were affected to some degree by the steric influence of the substituent in the 3-position. Although formation of all pyridylsulfur trifluoride intermediates was generally demonstrated (by ^{19}F NMR) after few hours of reaction, the rate of further transformation into the desired 2-pyridyl-SF_4Cl compounds depended greatly on the size of the substituent. Thus, disulfide **1i**, with the smallest *ortho*-fluoro substituent, was fully converted into 2-pyridyl-SF_4Cl **2i** after 72 h, with no residual SF_3-intermediate remaining. With increasing *ortho*-substituent size (3-F < 3-Me < 3-Cl < 3-Br), the conversion rate of the pyridylsulfur trifluorides into the respective pyridylsulfur chlorotetrafluorides decreased dramatically and could not be improved by increasing the reaction temperature, adding additional equivalents of KF and Cl_2, or prolonging the reaction time (Table 1).

Table 1: Reactivity of 3-substituted disulfides **1b**, **f**–**h**.

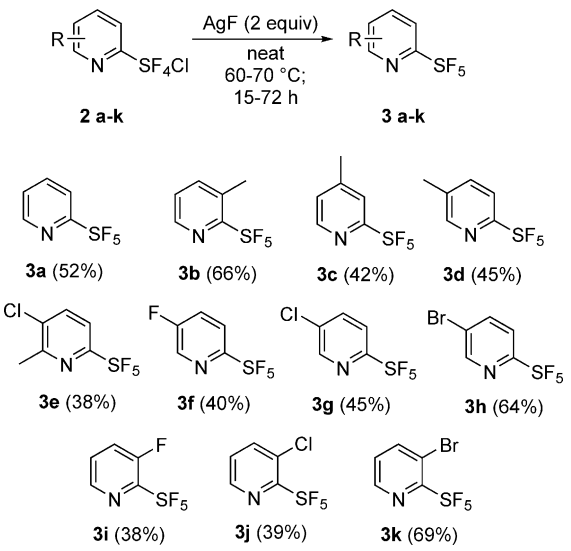


3-substituted disulfide reagent	Reaction products ratio (SF_3/SF_4Cl)
1f (R = F)	0/100
1b (R = Me)	35/65
1g (R = Cl)	50/50
1h (R = Br)	80/20

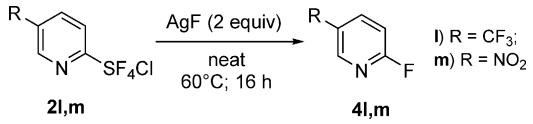
Rapid isolation, which included filtration under dry nitrogen pressure and solvent evaporation in vacuo, provided crude pyridylsulfur chlorotetrafluorides **2a**, **c**, **d**, and **f**–**i** with purities in the range of 80–95%. Immediately after isolation, the crude products were transferred into a fluoropolymer vial for the final fluorination step, which involved reaction with AgF. The 3-substituted pyridylsulfur chlorotetrafluorides **2b**, **j**, and **k** were isolated as mixtures with the corresponding pyridylsulfur trifluorides and used as is in their reactions with AgF. The pyridylsulfur trifluorides did not undergo reaction under these conditions. All chlorine–fluorine exchange reactions were done under an inert atmosphere using AgF (2 equiv) in a closed, flat-bottomed PFA vial without any solvent. After addition of the solid AgF, the vial was sealed and placed onto a hot plate preheated to 60–70 °C, The progress of the reaction was monitored by ^{19}F NMR spectroscopy until the complete consumption of the starting material pyridylsulfur chlorotetrafluoride was observed. The 2-SF_5-pyridines **3a**–**k** were isolated after partitioning the reaction mixtures between water and CH_2Cl_2 followed by filtration of the inorganic solids and recovering crude material by evaporation of the CH_2Cl_2 extracts. Further purification by column chromatography eluting with pentane/CH_2Cl_2 mixtures provided 38–69% yields of the pure 2-SF_5-pyridine derivatives. We believe that the high volatility of 2-SF_5-pyridines contributed to the relatively low yields that were obtained (Scheme 3).

The SF_4Cl group in pyridines **2l** and **2m**, which bear a strong electron-withdrawing substituent in the 5-position, was highly activated towards S_NAr reaction with fluoride anions, a process that competed very favorably with the desired final Cl–F exchange reaction. Thus, for those SF_4Cl compounds, conversion into the known 2-fluoropyridines **4l**[10] and **4m**[11] was detected, with little or no SF_5 product being formed (Scheme 4).

Under the same oxidative fluorination conditions, 3,3′-dipyridyl disulfide and 4,4′-dipyridyl disulfide did not form the corresponding pyridylsulfur chlorotetrafluorides. 3,3′-dipyridyl disulfide readily forms 3-pyridylsulfur trifluoride, which, in the presence of an excess of chlorine in the reaction mixture, underwent C–S bond cleavage much faster than the formation of the more stable 3-pyridylsulfur chlorotetrafluoride. In case of 4,4′-dipyridyl disulfide, C–S bond chlorinolysis is even faster and neither 4-pyridylsulfur trifluoride nor 4-pyridylsulfur chlorotetrafluoride could be detected in the reaction mixture. Instead, in both cases



Scheme 3. Synthesis of 2-pyridylsulfur pentafluorides **3 a–k**.



Scheme 4. Substitution reaction of 2-pyridyl chlorotetrafluorides **2l** and **2m** with AgF.

formation of gaseous products, such as SOF_2 ($\delta_F = +77$ ppm), SO_2F_2 ($\delta_F = +34$ ppm), and SF_5Cl ($\delta_F = +65$ ppm (p, $^2J_{F\text{-}F} = 150$ Hz, 1F), and $+125$ ppm (d, $^2J_{F\text{-}F} = 150$ Hz, 4F)) was detected in ^{19}F NMR spectra of the reaction mixtures as a result of C–S bond cleavage.

In conclusion, it has been demonstrated that excess oxidative fluorination of 2,2′-dipyridyl disulfides applying the KF/Cl_2/MeCN synthetic method provides ready access to 2-pyridylsulfur chlorotetrafluorides. These compounds can then be transformed into stable 2-SF_5-pyridines using silver(I) fluoride, which is a moderately expensive[12] but highly efficient and, in this case, essential, electrophilic chlorine–fluorine exchange reagent.

Investigations of possible applications of this method towards the preparation of other types of heterocyclic systems as well as explorations of reactivity of newly synthesized 2-pyridylsulfur chlorotetrafluorides and 2-SF_5-pyridines are currently underway in our laboratory.

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