Synthetic Methods

International Edition: DOI: 10.1002/anie.201710186
German Edition: DOI: 10.1002/ange.201710186

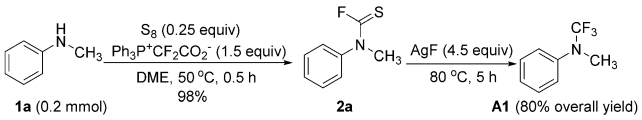
Reaction of Thiocarbonyl Fluoride Generated from Difluorocarbene with Amines

Jiao Yu, Jin-Hong Lin, and Ji-Chang Xiao**

Abstract: *The reaction of thiocarbonyl fluoride, generated from difluorocarbene, with various amines under mild conditions is described. Secondary amines, primary amines, and o-phenylenediamines are converted to thiocarbamoyl fluorides, isothiocyanates, and difluoromethylthiolated heterocycles, respectively. Thiocarbamoyl fluorides were further transformed into trifluoromethylated amines by using a one-pot process. Thiocarbonyl fluoride is generated in situ and is rapidly fully converted in one pot under mild conditions; therefore, no special safety precautions are needed.*

Difluorocarbene is a valuable and versatile intermediate in organic synthesis, particularly for fluorine incorporation.[1] Recently, we described the use of difluorocarbene generated from $Ph_3P^+CF_2CO_2^-$ (PDFA), a reagent that was developed by our group[2] and has also been used by other groups,[3] as a key intermediate for the challenging ^{18}F-trifluoromethylthiolation.[2c,f] Our mechanistic investigations of trifluoromethylthiolation showed that the key process is the reaction of difluorocarbene with elemental sulfur (S_8) to produce thiocarbonyl fluoride ($CF_2{=}S$),[2f] a transformation that has never been reported before. Although thiocarbonyl fluoride is an important fluorinated material, its use in synthetic chemistry remains largely unexplored because its preparation usually requires the use of hazardous reagents (such as thiophosgene) and/or harsh reaction conditions (e.g., pyrolysis at 500 °C). Furthermore, special safety precautions must be taken during storage and transfer of thiocarbonyl fluoride because of its high toxicity and low boiling point (−54 °C).[4] Our protocol for the use of thiocarbonyl fluoride is convenient and promising because thiocarbonyl fluoride is generated in situ and rapidly fully converted in one pot under mild conditions. Successful use of thiocarbonyl fluoride in reaction with oxygen nucleophiles[2g] prompted us to investigate nitrogen nucleophiles, such as unprotected amines.

Our initial reaction of secondary amine **1a** with thiocarbonyl fluoride generated from the PDFA/S_8 system gave thiocarbamoyl fluoride **2a** (Scheme 1). A brief survey of the reaction conditions (see the Supporting Information for details) showed that the conversion proceeded smoothly using 1.5 equivalents of PDFA and 0.25 equivalents of S_8 in 1,2-dimethoxyethane (DME) at 50 °C. After complete consumption of amine **1a**, the addition of AgF in a one-pot process resulted in desulfurization–fluorination of **2a** to afford trifluoromethyl amine **A1** in high yield (80 % overall yield).[5] Despite recent important achievements in CF_3 incorporation,[6] construction of the NCF_3 moiety remains challenging. Traditional synthetic methods, such as deoxy(sulfur)–fluorination or halogen–fluorine exchange reactions, suffer from tedious procedures or the use of hazardous reagents (SF_4, BrF_3, or HF).[7] Although electrophilic, radical, and nucleophilic trifluoromethylation approaches are effective,[8] CF_3-substituted free amines cannot be easily obtained by using these approaches because the nitrogen atom in NCF_3 must, usually, be attached to another heteroatom (nitrogen, oxygen, or sulfur)[8c–f] or because the trifluoromethylation reagent is unstable and highly reactive.[8a]



Scheme 1. Reaction of thiocarbonyl fluoride with a secondary amine and subsequent fluorination in one pot. Yields were determined by ^{19}F NMR spectroscopy.

With the optimized reaction conditions in hand, we investigated the substrate scope of the one-pot reaction of thiocarbonyl fluoride with secondary amines and subsequent desulfurization–fluorination (Table 1). Various N−aryl-N−alkyl amines were converted to the desired products in high yields irrespective of whether the aryl groups contained electron-rich, -neutral, or -deficient substituents (**A1**–**A21**). *N*,*N*-Diphenyl amine was not suitable for this reaction because of the low nucleophilicity of the amino group (**A22**). The conversion of *N*,*N*-dialkyl amines proceeded smoothly to furnish the expected products in high yields (**A23**–**A32**). The stabilities of **A23**–**A32** depend significantly on the electronic effects of the substituents. The alkyl groups in the *N*,*N*-dialkyl amines must be attached to electron-withdrawing groups, such as Ph (**A23** and **A24**), CO_2Et (**A23**), or CH_2NR' (**A26**–**A30**); otherwise, the products decompose easily and, therefore, cannot be isolated by using flash column chromatography (**A25**, **A31**, and **A32**). *N*,*N*-Dialkyl CF_3-amines readily undergo fluorine elimination because of n(N)→σ*(C−F) electron donation. This decomposition process was retarded by introducing electron-withdrawing groups into the alkyl groups. The formation of heterocycle-containing amines (**A20**–**A21** and **A26**–**A30**) may find utility in biochemistry.

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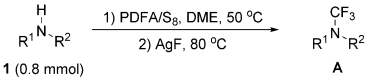
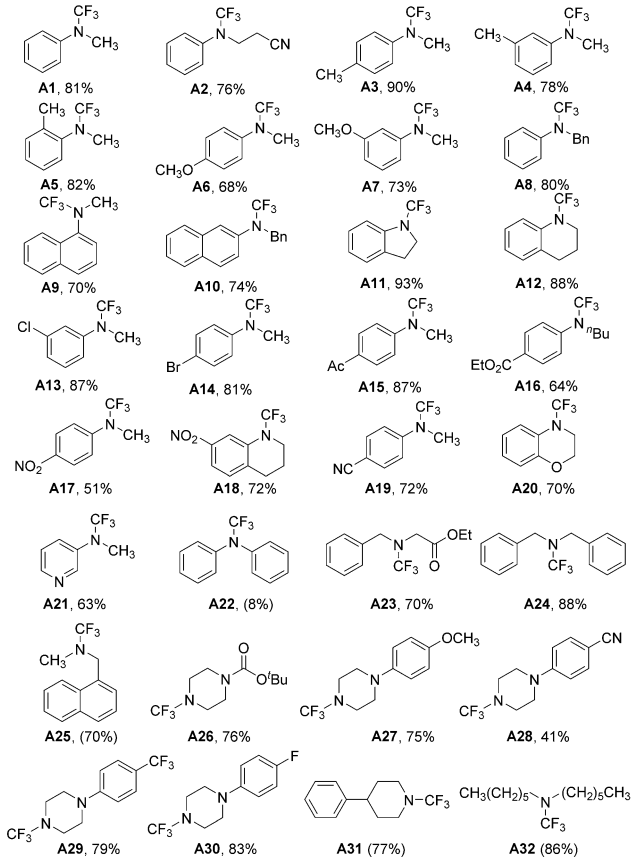
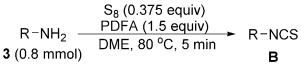
Table 1: Substrate scope for the one-pot reaction of thiocarbonyl fluoride with secondary amines and subsequent fluorination.

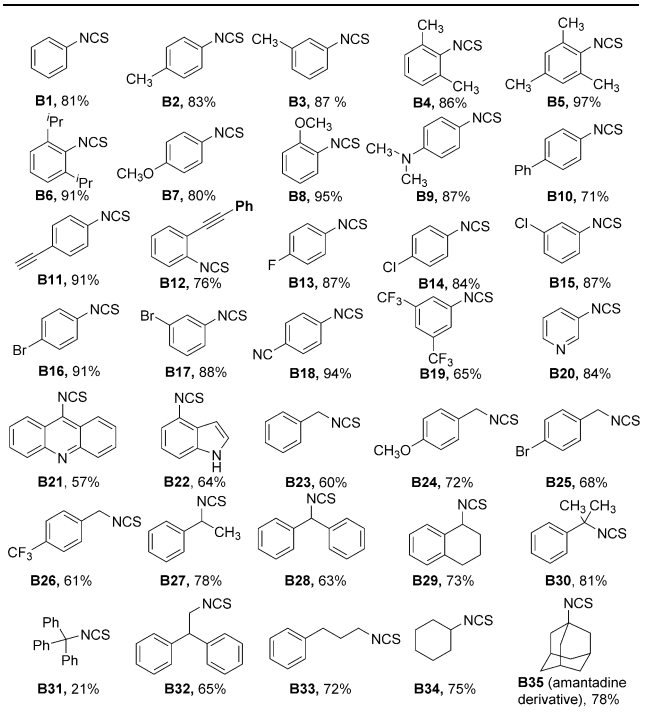




Yields of isolated products are shown. The yields in parentheses were determined by using ^{19}F NMR spectroscopy. Reaction conditions: **1** (0.8 mmol), PDFA (1.5 equiv), and S_8 (0.25 equiv) in DME at 50 °C for 0.5 h in a N_2 atmosphere. AgF (4.5 equiv) was then added and the resulting mixture was stirred at 80 °C for 5 h.

Table 2: Reaction of thiocarbonyl fluoride with primary amines. Isolated yields.

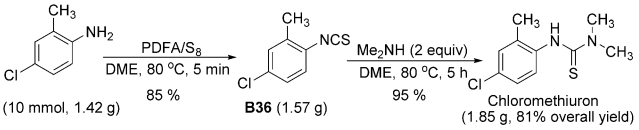




Reaction conditions: **3** (0.8 mmol), PDFA (1.5 equiv), and S_8 (0.375 equiv) in DME at 80 °C for 5 min in a N_2 atmosphere.

The successful reaction of thiocarbonyl fluoride with secondary amines prompted us to investigate its reaction with primary amines. It was found that the PDFA/S_8 system converted primary amines to isothiocyanates instead of thiocarbamoyl fluorides. All of the reactions of primary amines were fast (5 min) in DME at 80 °C as shown in Table 2. Various arylamines were converted to the desired products in high yields and with a high level of functional-group tolerance (**B1**–**B19**). Investigation of the electronic effects showed that neither electron-rich nor electron-withdrawing groups suppressed the desired conversion. Gratifyingly, heteroaryl amines were suitable for this transformation (**B20**–**B22**). The reaction is not sensitive to steric effects, as shown by the high yields of sterically hindered products **B4**–**B6** and **B21**. We previously reported that an alkynyl group can undergo [2+1] cyclization with difluorocarbene generated from PDFA;[2d] however, in this reaction the alkynyl group remained intact, confirming high functional-group compatibility (**B11** and **B12**). The transformation of amines containing a basic group, such as a tertiary amino (**B9**) or pyridinyl group (**B20**–**B21**), also proceeded smoothly. The tertiary amine group remained intact under these conditions (**B9**), although both primary and secondary amines are highly reactive towards thiocarbonyl fluoride. The yields of the desired products obtained from the reactions of alkyl amines (**B23**–**B35**) were lower than the product yields from arylamines. The reactions proceeded smoothly irrespective of whether the carbon atom attached to the amino group was a primary (**B23**–**B26**, **B32**, and **B33**), secondary (**B27**–**B29** and **B34**), or tertiary carbon center (**B30**, **B31** and **B35**). This finding indicates that steric hindrance did not affect the reactions of alkyl amines. Amantadine is an antiviral and antiparkinsonian drug that has been approved by the U.S. Food and Drug Administration. The isothiocyanate derivative of this drug was easily obtained by the strategy described herein (**B35**). Isothiocyanates occur widely in nature and are of interest in various areas, such as food science, medicine, and synthetic chemistry.[9] This convenient protocol has a wide range of potential applications for the synthesis of isothiocyanates.

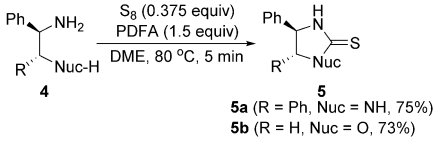
A convenient route to the insecticide chloromethiuron (CAS registry number: 28217-97-2) from a commercially available amine was developed to show the synthetic utility of this strategy for the conversion of primary amines (Scheme 2). The formation of isothiocyanate **B36** was fast,



Scheme 2. Synthesis of chloromethiuron.

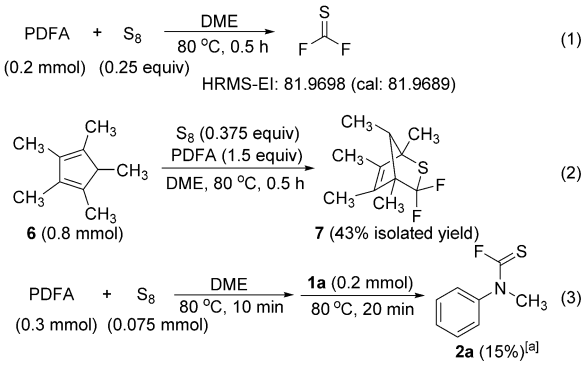
although the scale of the reaction was increased to 10 mmol. A high overall yield (81%) was obtained by means of a two-step procedure.

As shown in Scheme 2, the acyclic thiourea motif was constructed in two steps. It is reasonable to assume that only one step would lead to a cyclic thiourea if two amino groups are present in the substrate. This was confirmed by the rapid conversion of the vicinal diamine **4a** to cyclic thiourea **5a** (Scheme 3). Replacing one amino group with a hydroxy group gave oxazolidinethione **5b** in 73% yield. Thioureas[10] and oxazolidinethiones[11] are extensively used in medicinal chemistry and catalysis, therefore, the present protocol will be of great synthetic utility.



Scheme 3. Reaction of thiocarbonyl fluoride with vicinal diamine and vicinal hydroxyl amine.

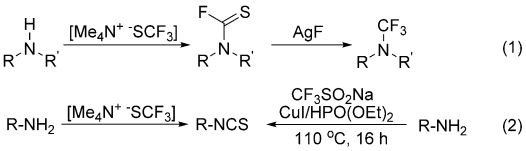
Thiocarbonyl fluoride generated from the PDFA/S_8 system is the key intermediate in the conversion of both primary and secondary amines. Simply heating a mixture of PDFA/S_8 in DME produces CF_2=S, as confirmed by using HRMS(EI) spectroscopy [Scheme 4, Eq. (1)]. The reaction of conjugated diene **6** with the PDFA/S_8 system generates a CF_2S-containing bridged compound [**7**, Scheme 4, Eq. (2)]. This bridged compound is formed by a Diels–Alder reaction of diene **6** with CF_2=S produced in situ. Furthermore, addition of substrate **1a** after complete consumption of PDFA by heating the PDFA/S_8 mixture at 80°C still gave the desired



Scheme 4. Generation and detection of CF_2=S. [a] Yield determined by using ^{19}F NMR spectroscopy.

thiocarbamoyl fluoride **2a** in 15% yield [Scheme 4, Eq. (3)]. This low yield can be explained by side reactions of CF_2=S in the absence of a substrate because of its high reactivity.

Recently, Schoenebeck and co-workers reported an excellent procedure for the synthesis of trifluoromethyl amines and isothiocyanates from the reaction of [Me_4N^+ CF_3S^-] with secondary [Scheme 5, Eq. (1)][5b] and primary

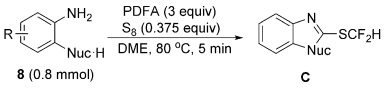


Scheme 5. Recently reported methods for incorporation of the CF_3 group and isothiocyanation.

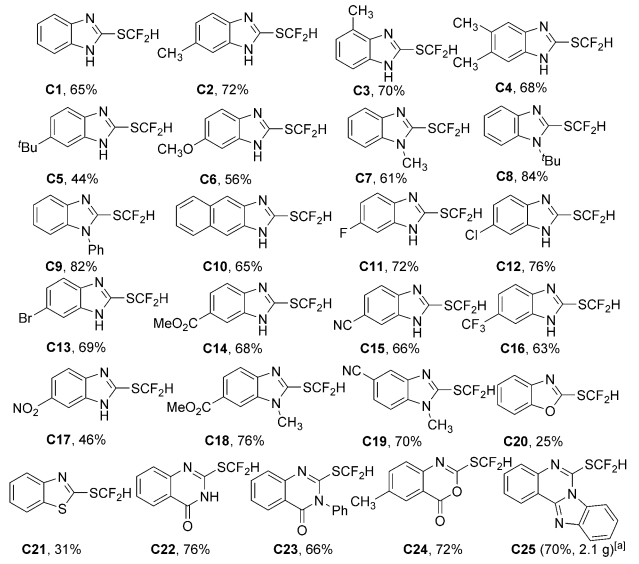
[Scheme 5, Eq. (2)] amines.[12] Thioureas could also be obtained if two amino groups were present in the substrates.[12] Their strategy for the synthesis of trifluoromethyl amines, pioneering work involving a one-pot-two-step transformation, is attractive owing to a rapid reaction process, a wide substrate scope, and a simple purification procedure.[5b] Thiocarbonyl fluoride is not the intermediate in the reaction reported by Schoenebeck and co-workers.[5b,12] During the preparation of this manuscript, Zheng and co-workers reported that Langlois reagent (CF_3SO_2Na) can also participate in isothiocyanation of primary amines in the presence of CuI/$HPO(OEt)_2$ [Scheme 5, Eq. (2)].[13] Although it was proposed that thiocarbonyl fluoride is one of the key intermediates, no direct evidence was observed. This approach suffers from a narrow substrate scope (limited suitability of alkyl amines), low functional-group tolerance (e.g., pyridinyl and terminal alkynyl groups are not tolerated), and the need for a long reaction time (16 h).

The HCF_2S-substituted benzimidazole **C1** (18% yield) was obtained from conversion of vicinal phenylenediamine **8a** under the same reaction conditions as for the reaction of a vicinal diamine in Scheme 3. This unexpected product was formed by means of a tandem cyclization/difluoromethylation process (for the proposed mechanism and experimental evidence, see the Supporting Information). After identification of the optimum conditions (see the Supporting Information), we explored the substrate scope for the reaction of thiocarbonyl fluoride with *o*-phenylenediamines or vicinal hydroxy (or amino) arylamines. As shown in Table 3, all of the reactions occurred rapidly (5 min) to furnish the desired HCF_2S heterocycles in good yields. The electronic effects of the substituents in various *o*-phenylenediamines (**C1–C19**) were investigated. Although electron-withdrawing groups decrease the nucleophilicity of the amino group, substrates containing electron-withdrawing groups were converted smoothly to form the desired HCF_2S-substituted benzimidazoles (**C11–C19**). Replacing one of the amino groups with a hydroxy or thiol group afforded the HCF_2S-substituted benzoxazole (**C20**) and benzothiazole (**C21**), respectively, but the yields were lower because of the lower nucleophilicity of hydroxy and thiol groups. As well as five-membered hetero-

Table 3: Reaction of thiocarbonyl fluoride with *o*-phenylenediamines or vicinal hydroxyl (or amino) arylamines and isolated yields.



8 (0.8 mmol) **C**



Reaction conditions: **8** (0.8 mmol), PDFA (3 equiv), and S_8 (0.375 equiv) in DME at 80 °C for 5 min in a N_2 atmosphere. [a] The reaction was performed on a 10 mmol scale. A reaction time of 10 min was required.

cycles (**C1**–**C21**), six-membered heterocycles were formed using this strategy (**C22**–**C25**). When the *ortho* substituent of the amino group was an amide or carboxylic acid group, HCF_2S-substituted 4-quinazolinone (**C22** and **C23**) and 3,1-benzoxazin-4-one (**C24**), respectively, were obtained. The imidazole NH group was able to act as a nucleophilic site to form a bridged ring (**C25**). Increasing the scale of the reaction to 10 mmol still afforded the desired product **C25** in good yield (70%), which demonstrates the synthetic utility of this tandem strategy. Although the heterocyclic NH group is a potential reactive site for difluoromethylation with difluorocarbene,[2d] the NH moieties in the above products remained intact, enabling further transformations. The structures of products **C6**[14] and **C23**[15] were confirmed by using X-ray diffraction (see the Supporting Information).

Heterocyclic compounds are important in many areas of life sciences.[16] The construction and structural modification of heterocycles have, therefore, attracted much attention from the chemical community.[17] The HCF_2S group can act as a lipophilic hydrogen-bond donor, therefore its incorporation into a heterocycle profoundly changes the physiochemical properties of the target compound.[18] Biologically active HCF_2S-substituted heterocycles have been reported. For example, pyriprole, an insecticide for veterinary use on dogs against external parasites, contains a HCF_2S-pyrazole moiety.[18b] In recent years, much effort has focused on the development of efficient methods for the incorporation of HCF_2S functionalities into organic molecules;[19] however, the synthesis of HCF_2S-substituted heterocycles remains largely unexplored. Recent approaches, including radical difluoromethylation of heteroarenethiols[20] and direct difluoromethylthiolation,[21] are effective, but all methods require the use of heteroarenes as substrates. The above strategy is the first example of fast and convenient construction of heterocycles with further incorporation of a HCF_2S group.

In conclusion, we have described the reactions of thiocarbonyl fluoride, formed from difluorocarbene, with unprotected amines. Amines undergo different reactions depending on their structures. Secondary amines, primary amines, and *o*-phenylenediamines are converted to thiocarbamoyl fluorides, isothiocyanates, and HCF_2S-substituted heterocycles, respectively. Thiocarbamoyl fluorides were further transformed into CF_3-amines by using a one-pot process. Thiocarbonyl fluoride is generated in situ and is rapidly fully converted in one pot under mild conditions, therefore, no special safety precautions are needed. The convenient use of thiocarbonyl fluoride has potential synthetic applications in various research areas.

Acknowledgements

The authors thank National Basic Research Program of China (2015CB931903), the National Natural Science Foundation (21421002, 21472222, 21502214, 21672242), the Chinese Academy of Sciences (XDA02020105, XDA02020106), and Key Research Program of Frontier Sciences (CAS) (QYZDJ-SSW-SLH049) for financial support.

Conflict of interest

The authors declare no conflict of interest.

Keywords: amines · difluorocarbene · difluoromethylthiolation · fluorine · thiocarbonyl fluoride

How to cite: *Angew. Chem. Int. Ed.* **2017**, *56*, 16669–16673
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[14] CCDC 1576012 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Manuscript received: October 2, 2017
Revised manuscript received: November 14, 2017
Accepted manuscript online: November 16, 2017
Version of record online: November 30, 2017

