Novel Heterocyclization of Imidoyl Chlorides with Mercaptocarboxylic Acids

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Abstract: A convenient, one-step synthetic approach to fluoroalkyl-substituted 1,3-oxathiolanones and benzoxathianones, based on readily accessible *N*-acyl and *N*-sulfonyl imidoyl chlorides, has been developed. The novel heterocyclization involves previously unknown participation of the imidoyl carbon atom as a bifunctional 1,1-electrophile.

Key words: imidoyl chlorides, oxathiolanone, benzoxathianone, fluoroalkyl, cyclization

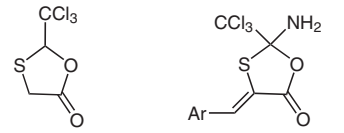
Imidoyl chlorides combine the properties of both acid chlorides and azomethines. They are reactive and versatile chemical agents that have found wide application in organic synthesis and in the study of chemical reactivity.[1] Trifluoroacetimidoyl chlorides are regarded as promising new building blocks for the synthesis of functionalized fluorine-containing compounds.[2]

Recently, we developed a syntheses of fluoro-[3] and trifluoroacetimidoyl chlorides,[4] containing electron-withdrawing acyl or sulfonyl groups at the nitrogen atom, that represent a new type of highly electrophilic fluorine-containing synthons.

We have already demonstrated the use of these compounds in the synthesis of biologically important acyclic and heterocyclic derivatives containing, simultaneously, fragments of aminophosphonic acids and trifluoromethyl, fluoro or difluoromethylene groups.[3–5]

Now we report a novel synthesis of oxathiolanones and oxathianones, with both fluoroalkyl substituents and an amine function at the carbon atom of the S–C–O sequence, based on heterocyclization of activated imidoyl chlorides.

Specifically, derivatives of 1,3-oxathiolanones have applications as fungicides, herbicides, growth regulators, precursors of modified nucleosides possessing antiviral properties,[6] and can be used for the introduction of α-mercaptocarboxylic acid fragments into peptides.[7] Related oxathiolanones, containing a trichloromethyl group at the C-2 atom, have proven to be plant growth regulators[6a,8] and enzyme inhibitors[6a–6c] (Figure 1). To the best of our knowledge, oxathiolanes containing both fluorinated substituents and an amino group at the C-2 atom, remain unknown.



Plant growth regulator Enzyme inhibitors

Figure 1 Some biologically active oxathiolanones

We present a convenient preparative method for the synthesis of oxathiolanones, based on accessible fluoroacetimidoyl chlorides, activated by *N*-acyl- or *N*-sulfonyl substituents. Thus, heterocyclization of imidoyl chlorides **1** with α-mercaptocarboxylic acids **2**, affords the corresponding oxathiolanones **3** in high yields (Table 1).

The method can be used for synthesis of oxathiolanones containing alkyl substituents with varying electron-withdrawing properties (CH_2F, CF_3) at the C-2 atom and either a sulfonyl, acyl or alkoxycarbonyl group at the nitrogen atom. The latter is important as removal of the N-protective groups can be accomplished under various conditions.

Previously known heterocyclizations involved participation of electrophilic (carbon atom) and nucleophilic (nitrogen atom) centers of C=N imine systems, interacting with the corresponding sites of bifunctional reagents.[1a,2] Indeed, common imines, on interaction with thioglycolates, either form stable addition products or undergo cyclization, through the C=N bond, to give thiazolidones.[9] Our strategy uses imidoyl chlorides as *1,1-electrophiles*, with the imine nitrogen atom not participating in heterocycle formation.

It is also notable that condensation of polyfluorocarbonyl compounds with mercaptocarboxylic acids allows the synthesis of oxathiolanones with only carbon-centered substituents at the C-2 atom.[7,10]

Virtually pure oxathiolanones **3** were obtained merely on mixing the reagents in an organic solvent at room temperature or brief heating. The unusually facile transformation of **1** to **3** most likely results from the highly electrophilic nature of imines **1** and from a beneficial, five-membered ring formation. The fact that interaction of **1** with β-mercaptopropionic acid leads to non-cyclic thioimidates **4** (Scheme 1), even upon prolonged heating or acidic catalysis, supports this assumption.

Since thioimidates **4** contain an activated azomethine bond and a peripheral carboxylic function, they can serve

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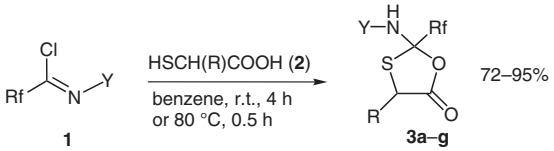
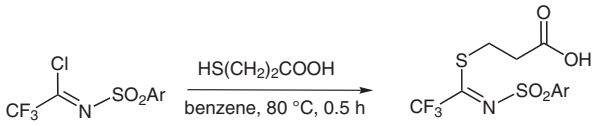
Table 1 Synthesis of Oxathiolanones **3**



Compound	Rf	R	Y	Isolated yield (%)
3a	CF_3	H	$PhSO_2$	95
3b	CF_3	H	Ts	95
3c	CF_3	CH_3	$PhSO_2$	92
3d	CF_3	CH_3	Ts	72
3e	CF_3	H	COOMe	76
3f	CF_3	H	C(O)Ph	86
3g	CH_2F	H	$C(O)CCl_3$	78

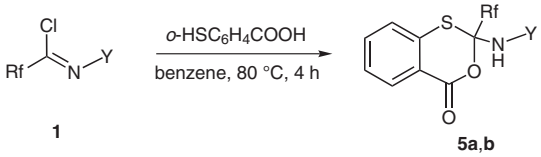


1a, **4a**: Ar = Ph
1b, **4b**: Ar = 4-MeC_6H_4

Scheme 1

as promising building blocks for the synthesis of functionally substituted, fluorine-containing compounds.

The position of the reactive centers is an important factor controlling ring closure. Thus, thiosalicylic acid, with a fixed *cis*-configuration of the HS- and HO- reactive centers, in contrast to β-mercaptopropionic acid, easily undergoes heterocyclization with imidoyl chlorides **1** to form 1,3-benzoxathian-4-ones **5** (Scheme 2).



5a: Rf = CF_3, Y = Ts
5b: Rf = CH_2F, Y = $CCl_3C(O)$

Scheme 2

Heterocyclic compounds **3**,**5** and thioimidates **4** are easily identified in the reaction mixture. The most important structural feature for identification is the fluorine chemical shift in ^{19}F NMR spectra (δ_F = –81 to –84 ppm for compounds **3**, **5** and –65 to –66 ppm for thioimidates **4**). The observed differences stem from the sp^3- and sp^2-hybridization of the carbon atom attached to the CF_3 group. Thus, transformation of **1** to **4** is accompanied by a downfield shift of the fluorine signals of the starting imidoyl chloride **1** (δ_F = –70 to –72 ppm), whereas the formation of heterocycles **3**, **5** results in an upfield displacement. Generation of a new chiral center upon formation of compounds **3**, **5** provides additional evidence that ring closure involves the imine carbon atom. This is clearly revealed in magnetic non-equivalence of diastereotopic hydrogen atoms of CH_2 group in the ^1H NMR spectra of compounds **3** and **5**. With R = Me, oxathiolanones **3c**,**d** are formed as a diastereomeric mixtures (1:1) that can be partially separated, in the case of **3c**, through fractional recrystallization.

It is important to note that the reactions studied here are all highly selective. Exclusively cyclic (**3**, **5**) or acyclic (**4**) compounds are formed, depending on the reagent structure. It is apparent that the transformation of **1** to **3** is a complex process, but we were unable to detect any intermediates spectroscopically. Only a decrease in intensity of the ^{19}F NMR signal of **1** accompanied by a corresponding increase of the respective signal of **3** was observed upon spectral monitoring of the reaction.

It is quite possible that substitution of the chlorine atom by the thio-function is accompanied by fast intramolecular ring closure of immonium salts of types *A* or *B* (Figure 2). The remarkable ease of heterocyclization can be explained by the high electrophilicity of the immonium C-atom and the geometrically favorable location of the reactive centers.

In summary, we have developed a simple and efficient synthesis of 1,3-oxathiolane-5-ones and 3,1-benzoxathian-4-ones, containing a protected amino function and a fluoroalkyl group at the C-2 atom of the heterocycle. A characteristic feature of the new heterocyclization is the fact that the imine carbon atom acts as a 1,1-electrophile, while the carboxylic group of the mercaptocarboxylic acid reacts through its O-nucleophilic center.

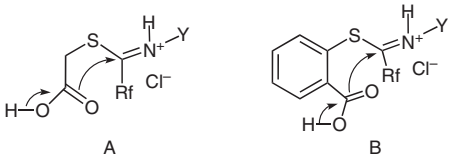


Figure 2

IR spectra were obtained with an UR-20 instrument in KBr pellets or as thin films. ^1H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer operating at 299.95 MHz, 282.20 MHz, and 75.43 MHz, respectively. Chemical shifts are reported relative to TMS (^1H, ^{13}C), or $CFCl_3$ (^{19}F) as the internal standards. Melting points are uncorrected. Solvents were dried before use according to standard methods.

Preparation of Compounds 3; General Procedure

To a stirred solution of the imidoyl chloride **1** (0.3 mmol) in benzene (5 mL), mercaptoacetic acid **2** (0.3 mmol) was added. After reacting for 4 h at r.t. or heating at 80 °C for 0.5 h, the solvent was evaporated under vacuum and the solid or oily residue was washed with hexane.

3a
White solid; mp 95–96 °C.

^{1}H NMR ($CDCl_3$): δ = 3.82 (d, $^2J_{HAHB}$ = 16.2 Hz, 1 H, CH_2), 4.03 (d, $^2J_{HBHA}$ = 16.2 Hz, 1 H, CH_2), 6.40 (s, 1 H, NH), 7.57 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, Ar), 7.64 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 7.94 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, Ar).

^{19}F NMR ($CDCl_3$): δ = –83.4.

Anal. Calcd for $C_{10}H_8F_3NO_4S_2$: C, 36.70; H, 2.46; N, 4.28; S, 19.59. Found: C, 36.74; H, 2.51; N, 4.22; S, 19.47.

3b
White solid; mp 137–139 °C.

IR (KBr): 1180, 1345 (S=O), 1820 (C=O), 3270 (NH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 3.81 (d, $^2J_{HAHB}$ = 16.2 Hz, 1 H, CH_2), 4.01 (d, $^2J_{HBHA}$ = 16.2 Hz, 1 H, CH_2), 6.19 (s, 1 H, NH), 7.35 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, Ar), 7.81 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, Ar).

^{13}C NMR ($CDCl_3$): δ = 21.6 (s, CH_3), 33.0 (s, CH_2), 93.0 (q, $^2J_{CF}$ = 35.8 Hz, CNH), 121.1 (q, $^1J_{CF}$ = 284 Hz, CF_3), 127.4, 129.8, 137.4, 144.9 (s, Ar), 168.5 (s, C=O).

^{19}F NMR ($CDCl_3$): δ = –83.5.

Anal. Calcd for $C_{11}H_{10}F_3NO_4S_2$: C, 38.71; H, 2.95; N, 4.10; S, 18.79. Found: C, 38.68; H, 2.90; N, 4.19; S, 18.75.

3c
Mixture of diastereomers *A* and *B* (1:2) was obtained after a single crystallization (benzene) of the 1:1 mixture.

White solid; mp 92–94 °C.

IR (KBr): 1180, 1360 (S=O), 1780 (C=O), 3310 (NH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.58 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH_3, *A*), 1.61 (d, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3, *B*), 4.16 (q, $^3J_{HH}$ = 6.7 Hz, 1 H, CH, *A*), 4.36 (q, $^3J_{HH}$ = 7.2 Hz, 1 H, CH, *B*), 6.43 (s, 1 H, NH, *B*), 6.49 (s, 1 H, NH, *A*), 7.56 [t, $^3J_{HH}$ = 7.8 Hz, 2 H (*A*) + 2 H (*B*), Ar], 7.66 [t, $^3J_{HH}$ = 7.8 Hz, 1 H (*A*) + 1 H (*B*), Ar], 7.92–7.96 (m, 2 H (*A*) + 2 H (*B*), Ar].

^{19}F NMR ($CDCl_3$): δ = –84.01 (*A*), –83.41 (*B*).

Anal. Calcd for $C_{11}H_{10}F_3NO_4S_2$: C, 38.71; H, 2.95; N, 4.10; S, 18.79. Found: C, 38.59; H, 2.97; N, 4.15; S, 18.68.

3d
Mixture of diastereomers *A* and *B* (1:1); white solid; mp 96–99 °C.

IR (KBr): 1180, 1360 (S=O), 1795 (C=O), 3310 (NH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.60 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH_3CH, *A*), 1.61 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH_3CH, *B*), 2.46 (s, 3 H, CH_3Ar, *A*), 2.48 (s, 3 H, CH_3Ar, *B*), 4.17 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, CH, *A*), 4.36 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, CH, *B*), 6.18 (s, 1 H, NH, *B*), 6.22 (s, 1 H, NH, *A*), 7.35 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ar, *A* or *B*), 7.40 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ar, *A* or *B*), 7.80 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ar, *A* or *B*), 7.82 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ar, *A* or *B*).

^{19}F NMR ($CDCl_3$): δ = –84.0 (*A*), –83.4 (*B*).

Anal. Calcd for $C_{12}H_{12}F_3NO_4S_2$: C, 40.56; H, 3.40; N, 3.94; S, 18.05. Found: C, 40.71; H, 3.37; N, 4.05; S, 18.12.

3e
Oil.

IR (film): 1750 (C=O), 1805 (C=O), 3340 (NH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 3 H, CH_3O), 3.88 (d, $^2J_{HAHB}$ = 16.2 Hz, 1 H, CH_2), 4.23 (d, $^2J_{HBHA}$ = 16.2 Hz, 1 H, CH_2), 6.37 (s, 1 H, NH).

^{19}F NMR ($CDCl_3$): δ = –83.0.

Anal. Calcd for $C_6H_6F_3NO_4S$: C, 29.39; H, 2.47; N, 5.71; S, 13.08. Found: C, 29.76; H, 2.59; N, 5.89; S, 12.97.

3f
White solid; mp 124–125 °C.

IR (KBr): 1660 (C=O), 1805 (C=O), 3220 (NH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.92 (d, $^2J_{HAHB}$ = 15.6 Hz, 1 H, CH_2), 4.29 (d, $^2J_{HBHA}$ = 15.6 Hz, 1 H, CH_2), 7.19 (s, 1 H, NH), 7.49 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Ar), 7.60 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, Ar), 7.77 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, Ar).

^{19}F NMR ($CDCl_3$): δ = –82.7.

Anal. Calcd for $C_{11}H_8F_3NO_3S$: C, 45.36; H, 2.77; N, 4.81; S, 11.01. Found: C, 45.51; H, 2.63; N, 4.92; S, 10.88.

3g
White solid; mp 105–106 °C.

IR (KBr): 1730 (C=O), 1795 (C=O), 3370 (NH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.83 (d, $^2J_{HAHB}$ = 16.2 Hz, 1 H, SCH_2), 4.31 (d, $^2J_{HBHA}$ = 16.2 Hz, 1 H, SCH_2), 4.67 (dd, $^2J_{HF}$ = 47.1 Hz, $^2J_{HAHB}$ = 10.8 Hz, H, FCH_2), 4.77 (dd, $^2J_{HF}$ = 47.1 Hz, $^2J_{HBHA}$ = 10.8 Hz, 1 H, FCH_2), 7.87 (s, 1 H, NH).

^{19}F NMR ($CDCl_3$): δ = –215.9 (t, $^2J_{FH}$ = 47.1 Hz).

Anal. Calcd for $C_6H_5Cl_3FNO_3S$: C, 24.30; H, 1.70; N, 4.72; Cl, 35.87; S, 10.81. Found: C, 24.42; H, 1.63; N, 4.83; Cl, 35.69; S, 10.92.

Preparation of Compounds 4; General Procedure
3-Mercaptopropionic acid **2** (0.3 mmol) was added to a stirred solution of the appropriate imidoyl chloride **1** (0.3 mmol) in benzene (5 mL). After reacting for 0.5 h at 80 °C, the solvent was evaporated in vacuum and the solid residue was washed with hexane.

4a
Yield: 93%; white solid; mp 110–112 °C.

IR (KBr): 1170, 1340 (S=O) 1595 (C=N), 1710 (C=O), 3200 (OH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.73 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, CH_2), 3.35 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, CH_2), 7.57 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, Ar), 7.66 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 7.99 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, Ar).

^{19}F NMR ($CDCl_3$): δ = –65.9.

Anal. Calcd for $C_{11}H_{10}F_3NO_4S_2$: C, 38.71; H, 2.95; N, 4.10; S, 18.79. Found: C, 38.64; H, 3.07; N, 4.26; S, 18.82.

4b
Yield: 82%; white solid; mp 114–115 °C.

IR (KBr): 1170, 1340 (S=O) 1595 (C=N), 1720 (C=O), 3260 (OH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 2.72 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, CH_2), 3.35 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, CH_2), 7.35 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, Ar), 7.87 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, Ar).

^{19}F NMR ($CDCl_3$): δ = –65.8.

Anal. Calcd for $C_{12}H_{12}F_3NO_4S_2$: C, 40.56; H, 3.40; N, 3.94; S, 18.05. Found: C, 40.71; H, 3.32; N, 4.08; S, 18.13.

Preparation of Compounds 5; General Procedure
Thiosalicylic acid (0.3 mmol) was added to a stirred solution of the appropriate imidoyl chloride **1** (0.3 mmol) in benzene (5 mL). After reacting for 4 h at 80 °C, the precipitate formed was filtered and washed with hexane.

5a

Yield: 95%; white solid; mp 180–181 °C.

IR (KBr): 1180, 1350 (S=O), 1745 (C=O), 3170 (NH) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 6.84 (s, 1 H, NH), 7.18 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 7.26 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, Ar), 7.38 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 7.54 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 7.70 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, Ar), 8.10 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar).

^{19}F NMR ($CDCl_3$): δ = –83.5.

Anal. Calcd for $C_{16}H_{12}F_3NO_4S_2$: C, 47.64; H, 3.00; N, 3.47; S, 15.90. Found: C, 47.84; H, 2.97; N, 3.51; S, 15.76.

5b

Yield: 96%; white solid; mp 169–170 °C (dec.).

IR (KBr): 1735 (C=O), 3300 (NH) cm^{-1}.

^1H NMR (DMSO-d_6): δ = 5.02 (d, $^2J_{HF}$ = 46 Hz, 1 H, FCH_2), 5.03 (d, $^2J_{HF}$ = 46 Hz, 1 H, FCH_2), 7.44 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 7.52 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 7.65 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 8.05 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, Ar), 10.80 (s, 1 H, NH).

^{19}F NMR (DMSO-d_6): δ = –222.1 (t, $^2J_{FH}$ = 46 Hz).

Anal. Calcd for $C_{11}H_7Cl_3FNO_3S$: C, 36.84; H, 1.97; Cl, 29.66; N, 3.91; S, 8.94. Found: C, 37.04; H, 2.13; Cl, 29.53; N, 4.02; S, 8.86.

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