Journal of Fluorine Chemistry 134 (2012) 160–163

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Electrophilic trifluoromethanesulfanylation of indole derivatives☆

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ARTICLE INFO

Article history:
Received 10 January 2011
Received in revised form 31 January 2011
Accepted 1 February 2011
Available online 26 February 2011

Keywords:
Trifluoromethanesulfanylamide
Fluorine
Aromatic electrophilic substitution
Trifluoromethylthio group
Indoles

ABSTRACT

Trifluoromethanesulfanylamides constitute a family of easily available reagents which could provide efficient ways to perform electrophilic trifluoromethanesulfanylation. In particular they are able to react with electron-rich aromatic compounds, more particularly with indoles, to yield expected CF_3S-subtituted molecules with good results.

1. Introduction

Because of the specific physico-chemical properties of fluorine [1,2], organofluorine chemistry has been steadily growing to become, today, a field of great importance with a distinctive role in highly diverse technological developments (fluoropolymers, pharmaceutical and agrochemical products, materials science, medical imaging, etc.) [3,4].

These last years, the association of a heteroatom with fluorinated groups has attracted a special interest. In particular the CF_3S moiety exhibits a high hydrophobicity parameter ($\pi_R = 1.44$) [5] and, thereby, compounds bearing this group are potentially important targets in the pharmaceutical and agrochemical fields [2(b,c),6].

Numerous methods are now available to introduce this function onto organic substrates, divided, essentially, into three distinct strategies [7]. The first one is the building of the CF_3S moiety by halogen–fluorine exchange reactions. This strategy is used on the industrial scale, but is generally limited to aromatic compounds [8]. The second method consists in grafting a CF_3 group onto a sulfur atom of the substrate. Such a strategy requires the preliminary synthesis of the sulfur-containing precursor. Trifluoromethylations of a sulfur atom have been essentially performed via nucleophilic [9] or radical trifluoromethylation [10] of disulfides, thiocyanates or thiols. A few electrophilic trifluoromethylations of thiols and thiolates have been also reported [11]. The most direct method remains the direct introduction of the CF_3S group onto molecules. Radical and electrophilic hydrogen substitutions have been essentially performed with CF_3SCl [12], which, however, is a very toxic reagent. Some nucleophilic reactions have been also realized by using stabilized forms of the unstable CF_3S anion, but, apart CF_3SCu whose reactivity is relatively limited [13o], such reagents are, generally, not stable enough to be stored for a long time [13].

Consequently, until recently, there was no efficient and easily available reagent to introduce directly a CF_3S moiety onto molecules by an electrophilic way.

2. Results and discussion

However, we have recently described an easy synthesis of trifluoromethanesulfanylamides (**1**) [14] and demonstrated that such compounds could react with alkenes and alkynes, under acidic activation, as an equivalent of the CF_3S^+ cation (Scheme 1) [15].

☆ *Description of the laboratory*: Our laboratory is involved in fluorine chemistry following three principal themes. The first one is a methodological aspect where we are interested in the development of new methods or reagents to introduce fluorine or fluorinated groups onto molecules. In particular, we focus our interest on the CF_3 moiety and on substituents associating CF_3 with heteroatoms (CF_3O, CF_3S, etc.). The second theme is devoted to the applications of our previous methodologies for the development of new fluorinated building-blocks and their application for the synthesis of potentially bioactive fluorinated compounds. Finally, we are also implied in medical imaging (PET scan) by developing new ligands, radiolabelled with ^{18}F nucleide, in particular for brain studies. For this purpose we develop also new methods of radiolabelling to introduce this radioisotope.

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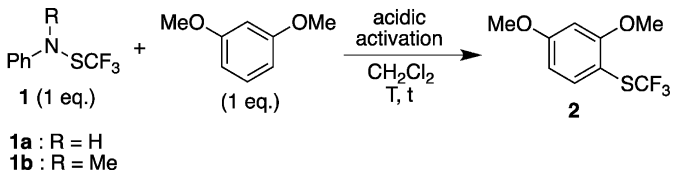
doi:10.1016/j.jfluchem.2011.02.005

Table 1
Trifluoromethanesulfanylation of 1,3-dimethoxybenzene.



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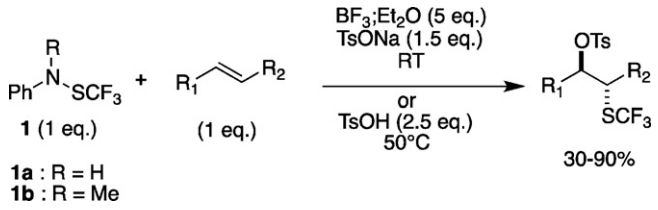
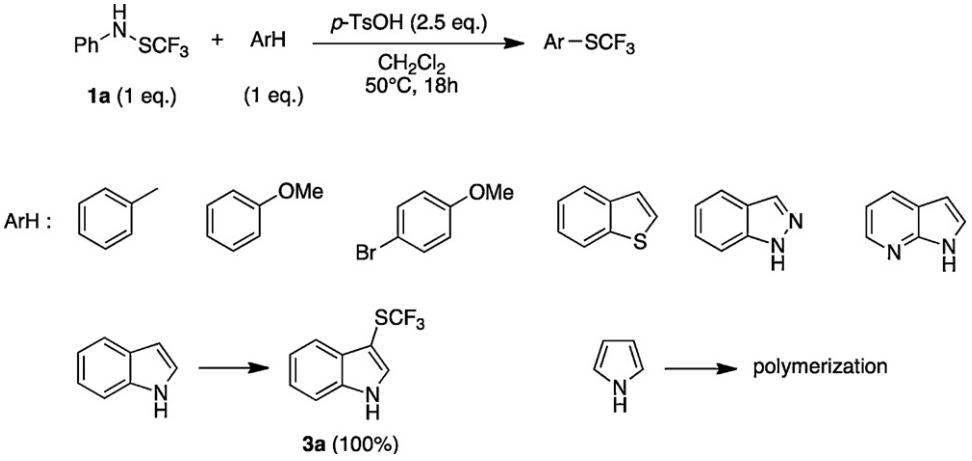
Entry	**1**	Acidic activation	*T* (°C)	*t* (h)	**2** Crude yield (%)[a]
1	**1a**	*p*-TsOH (2.5 eq.)	50	18	94
2	**1a**	BF_3;Et_2O (5 eq.)	RT	24	61
3	**1b**	BF_3;Et_2O (5 eq.)	RT	24	69

[a]Determined by ^{19}F NMR titration with internal standard ($PhOCF_3$).



Scheme 1. Trifluoromethanesulfanylation of alkenes with trifluoromethanesulfanylamides.



Scheme 2. Trifluoromethanesulfanylation of various aromatic compounds.

Since these reagents appear to be a powerful tool for electrophilic trifluoromethanesulfanylation, their use in electrophilic aromatic substitutions has been envisaged.

First attempts have been realized with 1,3-dimethoxybenzene as model substrate (Table 1).

All the conditions previously developed for the reaction of **1** with alkenes [15] have been tested. In contrast to alkenes, the best results were obtained under activation with protic acids instead of Lewis acids (Table 1, entry 1).

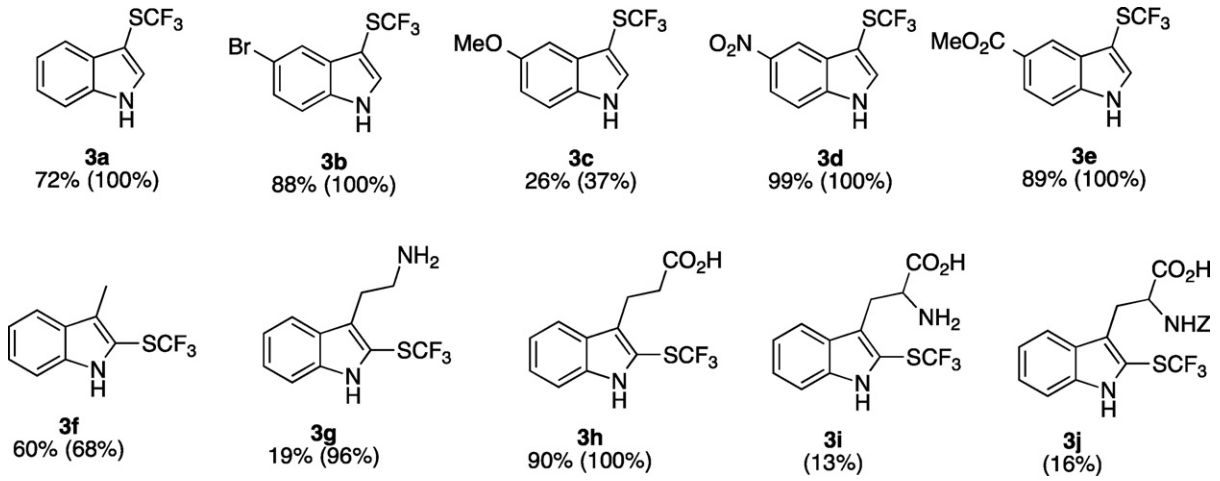
Under these selected conditions, other aromatic compounds have been engaged (Scheme 2).

The results were disappointing since, in general, no reaction have been observed, except with very electron-rich compounds, such as indole, which underwent trifluoromethanesulfanylation and led to the expected products. In the case of pyrrole, the acidic conditions have triggered off polymerization before the expected reaction took place.

Such results suggest that the reacting intermediate is not a real CF_3S^+ cation but a protonated form of **1a** which could be directly attacked by the nucleophile which displaces the anilino moiety and catches the CF_3S moiety. The low δ^+ polarization of the sulfur atom in such an intermediate could justify the need of very electron-rich aromatic substrates to perform the reaction.

Since indole itself gave good yield, various substituted indoles have been engaged in this reaction (Scheme 3).

In general, the expected products were obtained with good yields. It can be noticed that no protections of functional group are required (free NH indole, free NH_2 (**3g**), free CO_2H (**3h**)) to achieve good yields. When the 3-position of indole is already substituted, the 2-substitution is then observed (**3f**–**3j**). The low isolated yield observed with **3g** is essentially due to problems during extraction of the product from the crude mixture since the crude yield, observed by ^{19}F NMR, is excellent. More surprisingly, tryptophan did not give a good result (**3i**), whereas tryptamine (**3g**) and indole propionic acid (**3h**) led to good yields. The protection of the amino group of **3i** by a benzyloxycarbamate (**3j**) did not modify this disappointing result.



Scheme 3. Trifluoromethanesulfanylation of various indoles (in parentheses, crude yield determined by ^{19}F NMR titration with internal standard ($PhOCF_3$)).

3. Conclusion

Trifluoromethanesulfinamides (**1**) have confirmed their ability to realize electrophilic trifluoromethanesulfanylation and appear to be a good alternative to toxic CF_3SCl. Concerning electrophilic aromatic substitutions, the operating conditions have to be ameliorated to extend the panel of aromatic compounds to less electron-rich substrates. However, some CF_3S-substituted indoles have been already obtained with good yields and such products could already constitute interesting heterocyclic building-blocks for further syntheses of bioactive molecules.

4. Experimental

4.1. Typical procedure: synthesis of 2 or 3a–3f

To a solution of **1a** (1 mmol) in dichloromethane (2 mL) were added aromatic compounds (1 mmol) and then TsOH (2.5 mmol). The reaction mixture was heated for 18 h at 50 °C. The organic phase was washed with water and Et_2O and dried over Na_2SO_4. After removing solvent in vacuo, the crude was purified by flash chromatography.

4.2. 2,4-Dimethoxy-1-[(trifluoromethyl)thio]benzene (2)

Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (m, 1H), 6.54–6.50 (massif, 2H), 3.88 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 162.5, 140.6, 123.0 (q, $^1J_{C-F}$ = 309 Hz), 106.0, 103.6 (q, $^3J_{C-F}$ = 2.0 Hz), 99.6, 56.4, 55.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −44.12 (s). Anal. Calcd for $C_9H_9F_3O_2S$: C, 45.38; H, 3.81. Found: C, 45.16; H, 3.67.

4.3. 3-[(Trifluoromethyl)thio]-indole (3a) [12k]

Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.56 (bs, 1H), 7.80 (m, 1H), 7.53 (d, ^3J = 2.6 Hz, 1H), 7.42 (m, 1H), 7.32–7.24 (massif, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.5, 133.4 (q, $^4J_{C-F}$ = 1.1 Hz), 130.0 (q, $^1J_{C-F}$ = 310 Hz), 129.9, 123.8, 122.0, 119.7, 112.2, 95.7 (q, $^3J_{C-F}$ = 2.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ = −45.04 (s).

4.4. 5-Bromo-3-[(trifluoromethyl)thio]-indole (3b)

Brown solid. Mp = 48–49 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s large, 1H), 7.94 (m, 1H), 7.49 (d, ^3J = 2.8 Hz, 1H), 7.36 (dd, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 1H), 7.25 (dd, ^3J = 8.4 Hz, ^5J = 0.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.1, 134.2 (q, $^4J_{C-F}$ = 1.1 Hz), 129.7 (q, $^1J_{C-F}$ = 310 Hz), 131.6, 126.9, 122.3, 115.6, 113.7, 95.6 (q, $^3J_{C-F}$ = 2.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ = −44.87 (s). Anal. Calcd for $C_9H_5BrF_3NS$: C, 36.51; H, 1.70. Found: C, 36.68; H, 1.72.

4.5. 5-Methoxy-3-[(trifluoromethyl)thio]-indole (3c)

Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 7.49 (d, ^3J = 2.8 Hz, 1H), 7.30–7.26 (massif, 2H), 6.96 (m, 1H), 3.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 133.7 (q, $^4J_{C-F}$ = 1.1 Hz), 131.3, 130.7, 129.9 (q, $^1J_{C-F}$ = 310 Hz), 114.4, 113.0, 100.9, 95.4 (q, $^3J_{C-F}$ = 2.6 Hz), 56.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −43.50 (s). Anal. Calcd for $C_{10}H_8F_3NOS$: C, 48.58; H, 3.26. Found: C, 48.51; H, 3.17.

4.6. 5-Nitro-3-[(trifluoromethyl)thio]-indole (3d)

Yellow solid. Mp = 151–152 °C. ^1H NMR (300 MHz, acetone-d^6): δ = 11.69 (bs, 1H), 8.63 (m, 1H), 8.20 (d, ^3J = 2.3 Hz, 1H), 8.17 (m, 1H), 7.78 (m, 1H). ^{13}C NMR (75 MHz, acetone-d^6): δ = 143.9, 140.7, 139.1 (q, $^4J_{C-F}$ = 1.2 Hz), 130.3 (q, $^1J_{C-F}$ = 309 Hz), 129.9, 119.0, 115.9, 114.0, 96.6 (q, $^3J_{C-F}$ = 2.7 Hz). ^{19}F NMR (282 MHz, acetone-d^6): δ = −46.01 (s). Anal. Calcd for $C_9H_5F_3N_2O_2S$: C, 41.23; H, 1.92. Found: C, 41.36; H, 1.95.

4.7. Methyl-3-[(trifluoromethyl)thio]-1H-indole-5-carboxylate (3e)

White solid. Mp = 156–157 °C. ^1H NMR (300 MHz, acetone-d^6): δ = 11.39 (bs, 1H), 8.46 (m, 1H), 8.00 (d, ^3J = 2.8 Hz, 1H), 7.94 (dd, ^3J = 8.6 Hz, ^4J = 1.5 Hz, 1H), 7.65 (dd, ^3J = 8.6 Hz, ^5J = 0.7 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, acetone-d^6): δ = 167.8, 140.2, 137.2 (q, $^4J_{C-F}$ = 1.1 Hz), 130.5 (q, $^1J_{C-F}$ = 309 Hz), 130.0, 124.8, 124.4, 121.8, 113.3, 95.4 (q, $^3J_{C-F}$ = 2.6 Hz), 52.2. ^{19}F NMR (282 MHz, acetone-d^6): δ = −46.13 (s). Anal. Calcd for $C_{11}H_8F_3NO_2S$: C, 48.00; H, 2.93. Found: C, 48.07; H, 3.01.

4.8. 3-Methyl-2-[(trifluoromethyl)thio]-indole (3f)

Yellow solid. Mp = 95–96 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (bs, 1H), 7.70 (m, 1H), 7.44–7.37 (massif, 2H), 7.26 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 129.2 (q, $^1J_{C-F}$ = 312 Hz), 128.4, 125.6, 124.1 (q, $^4J_{C-F}$ = 1.1 Hz), 120.49, 120.47, 113.5 (q, $^3J_{C-F}$ = 2.4 Hz), 111.6, 9.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −43.50 (s). Anal. Calcd for $C_{10}H_8F_3NS$: C, 51.94; H, 3.49. Found: C, 51.90; H, 3.41.

4.9. 2-{2-[(Trifluoromethyl)thio]-1H-indol-3-yl}ethanamine (3g)

To a solution of **1a** (1 mmol) in dichloromethane (4 mL) was added tryptamine (1 mmol) then TsOH (2.5 mmol). The reaction

mixture was heated for 18 h at 50 °C. The reacting mixture was then filtered and the solid was washed with Et_2O. After removing solvent in vacuo, the filtrate was dissolved in CH_2Cl_2 and washed with aqueous $NaHCO_3$ (6%). The organic phase was dried over Na_2SO_4 and after removing solvent in vacuo, the crude was purified by flash chromatography (CH_2Cl_2/MeOH: 95/5 + 0.5% Et_3N).

Brown solid. Mp = 50–51 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.69 (bs, 1H), 7.65 (m, 1H), 7.36–7.25 (massif, 2H), 7.14 (m, 1H), 3.12–3.10 (massif, 4H), 2.27 (bs large, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 128.9 (q, $^1J_{C-F}$ = 312 Hz), 127.6, 125.0, 124.6 (q, $^4J_{C-F}$ = 1.1 Hz), 120.5, 120.3, 114.3 (q, $^3J_{C-F}$ = 2.4 Hz), 111.9, 42.7, 29.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −43.39 (s). Anal. Calcd for $C_{11}H_{11}F_3N_2S$: C, 50.76; H, 4.26; N, 10.76. Found: C, 51.11; H, 4.49; N, 11.04.

4.10. 3-{2-[(Trifluoromethyl)thio]-indol-3-yl}propanoic acid (3h)

To a solution of **1a** (1 mmol) in dichloromethane (2 mL) was added (3-propio)indolic acid (1 mmol) then TsOH (2.5 mmol). The reaction mixture was heated for 18 h at 50 °C. The reacting mixture was washed with H_2O. The organic phase was dried over Na_2SO_4 and after removing solvent in vacuo, the product **3h** is directly obtained.

Beige solid. Mp = 103–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (bs, 2H,), 7.66 (m, 1H), 7.40–7.29 (massif, 2H), 7.18 (m, 1H), 3.28 (t, ^3J = 8.0 Hz, 2H), 2.74 (t, ^3J = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.6, 138.0, 128.9 (q, $^1J_{C-F}$ = 311 Hz), 127.2, 125.7 (q, $^4J_{C-F}$ = 1.1 Hz), 125.3, 120.8, 120.2, 113.9 (q, $^3J_{C-F}$ = 2.4 Hz), 111.9, 35.1, 20.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −43.22 (s). Anal. Calcd for $C_{12}H_{10}F_3NO_2S$: C, 49.82; H, 3.48. Found: C, 50.05; H, 3.76.

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