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From carboxylic acids to the trifluoromethyl group using BrF_3

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ABSTRACT

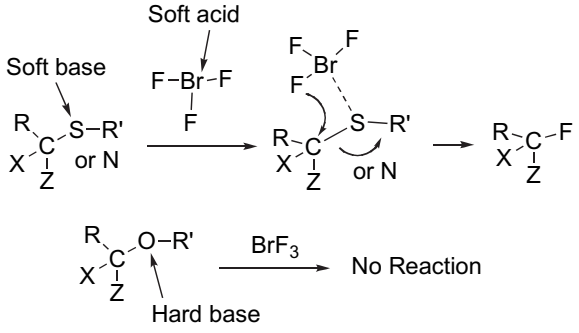
Organic trifluoromethyl derivatives were made from aromatic and aliphatic carboxylic acids by transforming them first into the corresponding dithioesters followed by reaction with bromine trifluoride under mild conditions (0 °C, 2 min).

1. Introduction

Compounds with the trifluoromethyl group enjoy high lipophilicity and increased stability compared to those with the methyl moiety and since, for many applications, the added steric distortion is not prohibitive, it is not surprising that this moiety can be found in various fields of organic chemistry especially in pharmaceuticals, anesthetics, agrochemicals, and polymers. Because of the intensive interest and high demand quite a few methods for the incorporation of the whole CF_3 group into organic molecules have been developed, such as using the popular Prakash–Rupert's reagent (CF_3SiMe_3),[1] fluoroform,[2] trifluoromethyl halides,[3] and electrophilic trifluoromethylations[4] to mention just a few. Sulfur tetrafluoride has also been used for constructing this desirable moiety.[5]

Bromine trifluoride is a commercial reagent, but because of its exothermic reactions with oxygen-containing solvents (see Experimental section) it has been rarely utilized by organic chemists.[6] Nevertheless, in the last years we have shown that when handled properly, it could be used under mild conditions for fast and selective reactions. We found that it can brominate aromatic rings, including very deactivated ones,[7] transfer carbonyls to the CF_2 group,[8] alcohols to trifluoromethyl or difluoromethyl ethers,[9,10] or under a different set of conditions to the corresponding acyl fluorides,[11] help in transforming RX to $RCHF_2$ derivatives,[12] and much more.[13]

The majority of the regiospecific reactions involving bromine trifluoride use the fact that the reagent's bromine atom is a soft acid, which can complex itself most effectively with soft bases, such as nitrogen or sulfur atoms, but not with hard ones, such as oxygen.[14] The complexation positions the nucleophilic fluorides near the potential reaction center resulting in an overall substitution of the nitrogen or sulfur atom(s) with fluorine (Scheme 1). Such complexation also reduces the chances of indiscriminate radical brominations and fluorinations for which this reagent was so infamous.[15]



Scheme 1. The complexation of BrF_3 with soft heteroatoms.

We describe in this work a new general method for transforming the aromatic and aliphatic carboxylic acid moiety into the important CF_3 group. This is accomplished by changing the hard basic oxygen with the soft sulfur atoms providing the much needed 'anchor' for the reagent enabling a selective reaction between the resulting dithioesters derivatives and BrF_3 for the eventual formation of the CF_3 products. Earlier results for fluorodesulforization processes with other [BrF] reagents (combination of two reactants, such as NBS and various forms of HF) were accomplished only with aromatic substrates.[16]

2. Results and discussion

Aromatic carboxylic acids **1** were converted to their acyl chlorides using oxalyl chloride, followed by a reaction with ethanethiol

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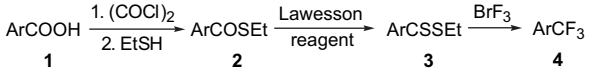
to form the appropriate thioesters **2**.[17] These thiocarbonyl containing derivatives were reacted with Lawesson reagent producing the corresponding dithioesters **3**, which were ready for the reaction with BrF_3. Thus, the dithioester of 4-cyanobenzoic acid **3a** was treated with 3 mole-equiv of bromine trifluoride for 2 min at 0 °C to give 4-(trifluoromethyl)benzonitrile (**4a**)[18] in 75% yield.[19] While BrF_3 is capable of transforming the nitriles themselves to CF_3 moieties,[20] the resulting **4a** suggests that the reaction with the dithioester group is more readily executed, since the soft–soft interaction between bromine and sulfur is better than bromine and nitrogen, so the cyano moiety was not affected (Table 1).

Table 1
Preparation of the trifluoromethyl moiety from benzoic acid derivatives



a	Ar=4-CNC_6H_4	95%	90%	75%
b	Ar=4-ClC_6H_4	95%	90%	70%
c	Ar=2-ClC_6H_4	95%	90%	70%
d	Ar=3-BrC_6H_4	95%	90%	75%
e	Ar=4-BrC_6H_4	95%	90%	75%
f	Ar=4-$CF_3C_6H_4$	95%	90%	65%
g	Ar=4-$HOOCC_6H_4$			
g′	Ar=4-$EtSSCC_6H_4$	95%	80%	30%

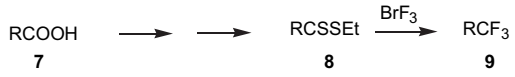
It is worth mentioning that BrF_3 also possesses the ability to exchange fluorine with other halogens.[21] As with the previous case, however, the halogen atom in the dithioesters of 4-chlorobenzoic acid (**1b**), 2-chlorobenzoic acid (**1c**), 3-bromobenzoic acid (**1d**), and 4-bromobenzoic acid (**1e**), remained intact during the reaction with bromine trifluoride, and the products **4b**–**e**[18] were obtained in 70–75% yields.

In general the best results in the aromatic field were obtained with compounds having a deactivated ring—a feature, which guards against aromatic electrophilic bromination. The deactivated 4-(trifluoromethyl)benzoic acid (**1f**), satisfies this requirement and eventually forms 1,4-bis(trifluoromethyl)benzene (**4f**)[18] in 65% yield. Alternatively this compound could be generated also from the terephtalic acid (**1g**), by converting it to its tetrathio diester **3g′** followed by a reaction with 6 mole-equiv of BrF_3 to form the expected **4f**. This result shows that the reaction is applicable also for cases where more than a single carboxylic acid group is present.

The reaction is not limited to aromatic carboxylic acids. Many aliphatic ones can serve as substrates as well. The dithioesters **8a** and **8b**, made from 2-hexyl-2-methyldecanoic acid (**7a**) and 2,2-dimethyldodecanoic acid (**7b**), were reacted with BrF_3 under the same mild conditions outlined above resulting in the previously unknown 7-methyl-7-(trifluoromethyl)pentadecane (**9a**) and 1,1,1-trifluoro-2,2-dimethyldodecane (**9b**) in 80 and 70% yield, respectively (Table 2). Cyclic carboxylic acids also work fine as can be demonstrated by 1-methyl-1-cyclohexanecarboxylic acid (**7c**), which was converted via its dithioester derivative (**8c**) to 1-methyl-1-trifluoromethylcyclohexane (**9c**)[22] in 80% yield.

In certain cases BrF_3 can be engaged in electrophilic fluorinations especially in the presence of tertiary hydrogen atoms.[23] Yet, when 1-adamantane carboxylic acid (**8d**) was reacted 1-(trifluoromethyl)adamantane (**9d**)[24] was formed without much electrophilic substitution of the tertiary hydrogens. This may point out to the substantial difference in the reactivity between centers that provide a strong anchor for the reagent (in our case sulfur atoms) and ones with much weaker complexation power.[25] The fast reaction completed under the mild conditions also ensures the integrity of the adamantane skeleton, which under harsh conditions, or strong oxidants, can undergo various rearrangements.[26]

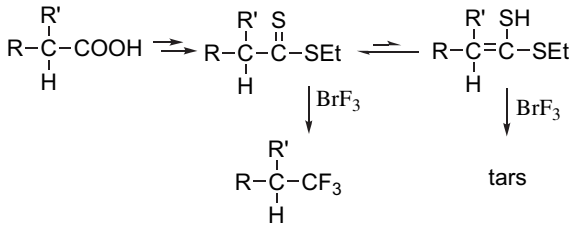
Table 2
Preparation of the trifluoromethyl moiety from aliphatic carboxylic acids



a	R = C_8H_{17}–CH(Me)–C_6H_{13}	70%	80
b	R = $C_{10}H_{21}$–C(Me)$_2$	90%	70%
c	R = 1-methylcyclohexyl	90%	80%
d	R = 1-adamantyl	95%	65%
e	R = (C_8H_{17})(C_6H_{13})CH–	85%	45%
f	R = (cyclohexyl)$_2$CH–	80%	40%
g	R = 2-adamantyl	80%	35%
h	R=$C_{11}H_{23}$–	90%	Traces

With secondary carboxylic acids the yields of transforming the COOH group to the CF_3 one are usually lower. This is evident from several results among them the cases of 7-pentadecanoic acid (**7e**), 2,2-dicyclohexylethanoic acid (**7f**), and 2-adamantanecarboxylic acid (**7g**), which were converted via their dithioesters **8e–g**, to the previously unknown, 7-trifluromethylpentadecane (**9e**), 1,1-dicyclohexyl-2,2,2-trifluoroethane (**9f**), and 2-(trifluoromethyl)adamantane (**9g**)[27] all in about 40% yield. This trend is even more profound with primary acids, where dodecanoic acid **7h** can serve as a typical example. The reaction of its dithioester **8h**[28] with BrF_3 resulted in a mixture containing only traces of the 1,1,1-trifluoroundecane (**9h**).

We believe the reason for the different behavior of tertiary (and aromatic), secondary and primary acids, is rooted in the fact that the secondary, and even more so primary, dithioesters are prompt to some degree toward tautomerism, which shifts the equilibrium slightly more toward the enthiol structure. Obviously such process cannot take place in the tertiary or aromatic derivatives. As we have shown in the past, bromine trifluoride reacts very fast with any type of double bond,[29] which in this case leads mainly to non-specific reactions (Scheme 2).



Scheme 2. The reaction with secondary and primary acid.

In conclusion, this work offers a new route for the formation of the important trifluoromethyl group derived from carboxylic acid derivatives using a simple sequence of reactions with the eventual use of BrF_3 as the source of the fluorine atoms. We hope that along with the new synthetic pathway, this work will contribute to reduce the recoil of many chemists from the thought of using

bromine trifluoride and that more people will start considering it when it comes to fluorination processes.

3. Experimental section

3.1. General

^{1}H NMR spectra were recorded using a 200 MHz spectrometer with $CDCl_3$ as a solvent and Me_4Si as an internal standard. The ^{19}F NMR spectra were measured at 188.1 MHz using $CFCl_3$ as an internal standard. The proton broadband decoupled ^{13}C NMR spectra were recorded at 100.5 MHz. Here too, $CDCl_3$ served as a solvent and Me_4Si as an internal standard. Mass spectra were measured under CI conditions. When EI conditions were needed we used Aviv Analytical 5975-SMB-supersonic GC–MS. The main feature of this method is to provide electron ionization while the sample is vibrationally cooled in a supersonic molecular beam. This considerably enhances the relative abundance of molecular ions.[30,31] All dithioesters were thus characterized using isotope abundance analysis to confirm the structure. This analysis confirmed the proposed elemental formulas as it ranked them all at the first place and hence, as the best choice with very good matching factors of better then 980 out of 999 (minimum match allowed 800).[32]

3.2. Preparation and handling of BrF_3

Although commercially available, we usually prepare BrF_3 by passing 0.6 mol fluorine through 0.2 mol of bromine placed in a copper reactor and held at temperatures between 0 and +10 °C. Under these conditions pure bromine trifluoride is obtained (can be checked either by its melting point of +9 °C, or boiling point of 126 °C) while the higher oxidation state of bromine, BrF_5, will not be formed in any appreciable amount.[33] The reagent can be stored in Teflon® containers indefinitely. BrF_3 is a strong oxidizer and tends to react very exothermically with water and oxygenated organic solvents, such as acetone or THF. Alkanes, like petrol ether, cannot serve as solvents either since they also react quickly with BrF_3. Solvents, such as $CHCl_3$, CH_2Cl_2, $CFCl_3$ or, if solubility is not an issue, any perfluoroalkane or perfluoroether can be used. Any work using BrF_3 should be conducted in a well ventilated area and caution and common sense should be exercised.

3.3. General procedure for the formation of *S*-ethyl ester

An acyl chloride (40 mmol) was added to a solution of Et_3N (1.3 mole-equiv) and ethanethiol (2.1 mole-equiv) in dry THF (100 mL). The reaction mixture was stirred under nitrogen overnight. The white precipitate was filtered and the organic layer concentrated to give the desired product in about 95% yield and was used without further purification. Typical ^{1}H NMR value for the SCH_2 group is δ 2.85 ppm (2H, q, J=7.5 Hz).

3.4. General procedure for the formation of dithioesters

Thioester (20 mmol) was dissolved in 20 mL of dry toluene. To this solution, Lawesson reagent (0.6 mole-equiv) was added and the suspension was refluxed under nitrogen for 16–20 h. The reaction progress was monitored by GC and after completion the suspension was cooled to room temperature and filtered. The filtrate was concentrated and flash chromatographed to give the desired dithioester. The aromatic dithioesters and **8h** are known and referenced. It should be noted, however, that while the purity of the thio and dithioesters achieved by this procedure was higher than 90%, no efforts to obtain analytical purity were made since the crude products were successfully used 'as is' for the next step.

*3.4.1. Ethyl 2-hexyl-2-methyl-decanedithionate (**8a**).* Compound **8a** was prepared from ethyl 2-hexyl-2-methyl-decanethionate as described above in 70% yield. ^{1}H NMR δ 3.16 (2H, q, J=7.4 Hz), 1.40 (3H, s), 1.31 (3H, t, J=7.4 Hz), 1.28–1.12 (24H, br s), 0.92–0.82 ppm (6H, m); MS calcd: 330. Found: (using supersonic molecular beam) (m/z) 330 $(M)^+$ with isotope abundance analysis matching factor of 996 out of 999.

*3.4.2. Ethyl 2,2-dimethyl-dodecanedithionate (**8b**).* Compound **8b** was prepared from ethyl 2,2-dimethyl-dodecanethionate as described above in 90% yield. ^{1}H NMR δ 3.17 (2H, q, J=7.5 Hz), 1.41 (6H, s), 1.32 (3H, t, J=7.5 Hz), 1.28–1.14 (18H, br s), 0.88 ppm (3H, t, J=6.9 Hz); MS calcd: 288. Found: (using supersonic molecular beam) (m/z) 288 $(M)^+$ with isotope abundance analysis matching factor of 992 out of 999.

*3.4.3. Ethyl 1-methyl-cyclohexanecarbodithionate (**8c**).* Compound **8c** was prepared from ethyl 1-methyl-cyclohexanecarbothionate as described above in 90% yield. ^{1}H NMR δ 3.19 (2H, q, J=7.3 Hz), 2.80–1.40 (13H, m), 1.31 ppm (3H, t, J=7.3 Hz); MSCI (m/z) 203 $(M+H)^+$.

*3.4.4. Ethyl 1-adamantanecarbodithionate (**8d**).* Compound **8d** was prepared from ethyl 1-adamantanecarbothionate as described above in 90% yield. ^{1}H NMR δ 3.16 (2H, q, J=7.4 Hz), 2.15 (9H, m), 1.72 (6H, m), 1.30 ppm (3H, t, J=7.4 Hz); MS calcd: 240. Found: (using supersonic molecular beam) (m/z) 240 $(M)^+$ with isotope abundance analysis matching factor of 980 out of 999.

*3.4.5. Ethyl 2-hexyl-decanedithionate (**8e**).* Compound **8e** was prepared from ethyl 2-hexyl-decanethionate as described above in 85% yield. ^{1}H NMR δ 3.23 (2H, q, J=7.5 Hz), 3.12 (1H, quin, J=5.0 Hz), 1.41 (6H, s), 1.31 (3H, t, J=7.5 Hz), 1.27–1.18 (24H, br s), 0.91–0.82 ppm (6H, m); MS calcd: 316. Found: (using supersonic molecular beam) (m/z) 316 $(M)^+$ with isotope abundance analysis matching factor of 993 out of 999.

*3.4.6. Ethyl dicyclohexyl-dithioacetate (**8f**).* Compound **8f** was prepared from ethyl dicyclohexyl–thioacetate as described above in 80% yield. ^{1}H NMR δ 3.19 (2H, q, J=7.5 Hz), 2.94 (1H, t, J=7.5 Hz), 2.22–0.82 ppm (25H, m); MS calcd: 284. Found: (using supersonic molecular beam) (m/z) 284 $(M)^+$ with isotope abundance analysis matching factor of 981 out of 999.

*3.4.7. Ethyl 2-adamantanecarbodithionate (**8g**).* Compound **8g** was prepared from ethyl 2-adamantanecarbothionate as described above in 75% yield. ^{1}H NMR δ 3.24 (2H, q, J=7.5 Hz), 2.84 (1H, m), 2.20–1.45 (14H, m), 1.32 ppm (3H, t, J=7.5 Hz); MS calcd: 240. Found: (using supersonic molecular beam) (m/z) 240 $(M)^+$ with isotope abundance analysis matching factor of 980 out of 999.

*3.4.8. Ethyl dodecanedithionate (**8h**)*[28]. Compound **8h** was prepared from ethyl dodecanethionate as described above in 90% yield.

3.5. General procedure for reacting dithioesters with BrF_3

Dithioester (1–10 mmol) was dissolved in 10–20 mL of $CFCl_3$ and cooled to 0 °C. About 3 mole-equiv of BrF_3 was dissolved in the same solvent, cooled to 0 °C and added dropwise to the reaction mixture during 2 min. After the addition was completed, the reaction was washed with aqueous $Na_2S_2O_3$ solution until colorless. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was dried over $MgSO_4$. Evaporation of the solvent followed by flash chromatography (using petroleum ether as eluent) gave the desired trifluoromethyl derivative. Products **4a** through **4f** are commercial and their spectroscopic data were identical to the corresponding authentic samples. The reactions leading to those compounds were performed on scale of 1.3–1.5 mmol of the corresponding dithioesters **3** with yields of 70–75% (see Table 1).

*3.5.1. 1,4-Bis(trifluoromethyl)benzene (**4f**).* Compound **4f** was prepared from **3f** (376 mg, 1.5 mmol) as described above in 65% yield. It was also prepared from **6** (430 mg, 1.5 mmol) and 6 mole-equiv of BrF_3 as described above in 30% yield.

*3.5.2. 7-Methyl-7-trifluoromethylpentadecane (**9a**).* Compound **9a** was prepared from **8a** (496 mg, 1.5 mmol) as described above in 80% yield as colorless oil. ^{1}H NMR δ 1.52–1.35 (4H, m), 1.27 (20H, br s), 1.04 (3H, s), 0.92–0.85 ppm (6H, m); ^{13}C NMR δ 130.6 (q, J=284 Hz), 43.4 (q, J=23 Hz), 34.5, 32.6, 32.4, 31.1, 30.8, 30.2, 30.0, 24.2, 23.4, 20.1, 14.8, 14.7 ppm; ^{19}F NMR δ −75.1 ppm (s); HRMS (CI) (m/z) calcd for $C_{17}H_{33}F_3$=293.2456 $(M-H)^+$, found 293.2455.

*3.5.3. 1,1,1-Trifluoro-2,2-dimethyldodecane (**9b**).* Compound **9b** was prepared from **8b** (433 mg, 1.5 mmol) as described above in 70% yield as colorless oil. ^{1}H NMR δ 1.48–1.39 (2H, m), 1.27 (16H, br s), 1.07 (6H, q, J=1 Hz), 0.88 ppm (3H, t, J=7 Hz); ^{13}C NMR δ 130.5 (q, J=283 Hz), 40.8 (q, J=24 Hz), 36.4, 32.6, 31.0, 30.4, 30.3, 30.2, 30.0, 24.2, 23.4, 21.2, 14.8 ppm; ^{19}F NMR δ −78.9 ppm (s); HRMS (CI) (m/z) calcd for $C_{14}H_{27}F_3$=251.1987 $(M-H)^+$, found 251.1981.

*3.5.4. 1-Methyl-1-trifluoromethylcyclohexane (**9c**)*[22]. Compound **9c** was prepared from **8c** (2.02 g, 10 mmol) as described above in 80% yield.

*3.5.5. 1-Trifluoromethyladamantane (**9d**)*[24]. Compound **9d** was prepared from **8d** (313 mg, 1.3 mmol) as described above in 65% yield.

*3.5.6. 7-Trifluoromethylpentadecane (**9e**).* Compound **9e** was prepared from **8e** (950 mg, 3 mmol) as described above in 45% yield as colorless oil. ^{1}H NMR δ 2.08–1.95 (1H, m), 1.65–152 (2H, m), 1.48–1.24 (22H, m), 0.95–0.87 ppm (6H, m); ^{13}C NMR δ 129.5 (q, J=280 Hz), 43.3 (q, J=25 Hz), 32.6, 32.3, 30.4, 30.1, 30.0, 28.6, 27.6, 23.4, 23.3, 14.8, 14.7 ppm; ^{19}F NMR δ −70.6 ppm (d, J=10 Hz); HRMS (CI) (m/z) calcd for $C_{16}H_{31}F_3$=279.2300 $(M-H)^+$, found 279.2298.

*3.5.7. 1,1-Dicyclohexyl-2,2,2-trifluoroethane (**9f**).* Compound **9f** was prepared from **8f** (428 mg, 1.5 mmol) as described above in 40% yield as colorless oil. δ_H 1.87–1.44 (13H, m), 1.39–1.00 ppm (10H, m); δ_C 129.6 (q, J=283 Hz), 54.7 (q, J=22 Hz), 37.9, 33.1, 31.3, 27.8, 27.7, 26.9 ppm; δ_F −61.6 ppm (d, J=12 Hz); HRMS (CI) (m/z) calcd for $C_{14}H_{23}F_3$=247.1674 $(M-H)^+$, found 247.1670.

*3.5.8. 2-Trifluoromethyladamantane (**9g**)*[27]. Compound **9g** was prepared from **8g** (962 mg, 4 mmol) as described above in 35% yield.

Acknowledgements

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