Photochemical Trifluoromethylation of 1-Methylimidazoles and 1-Methylpyrroles Containing Methylthio Groups

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The title reaction was achieved by UV (254 nm) irradiation with CF_3I. The methylthio group was introduced to increase electron density and to limit available reactive sites in the rings. Following trifluoromethylation, the methylthio groups were readily removed by hydrogenolysis (Raney Ni) to give the desired trifluoromethyl heterocycles.

Heterocyclic compounds containing the trifluoromethyl group are of considerable interest because of their utility as drugs and agricultural chemicals. Trifluoromethyl groups on imidazoles and pyrroles possess the additional property of undergoing facile transformations to other functional groups.[1)]

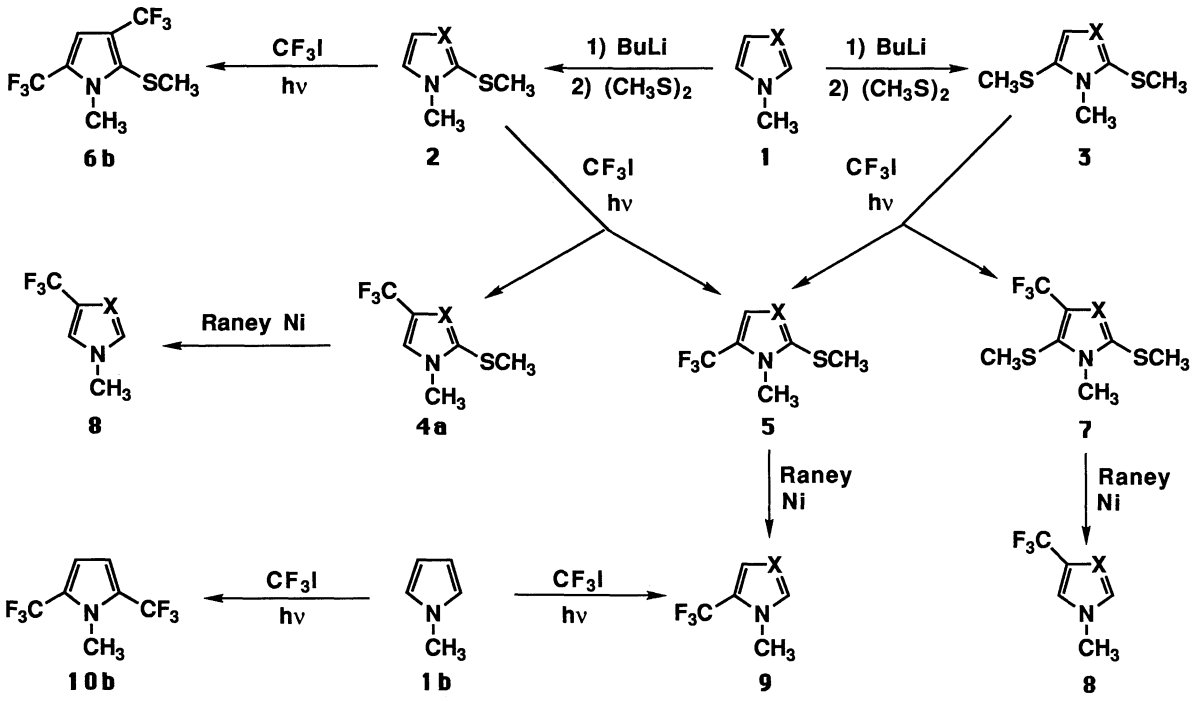
Regiospecific introduction of this group has been achieved by reaction of the carboxyl group with SF_4,[2a)] by reaction of hetaryl halides with trifluoromethyl organometallics,[2b)] by ring closure of 1,2-bis(acylamino)-ethylenes with trifluoroacetic anhydride[3)] and by ring closure involving various ketones.[4)] Of these methods, only the latter two can be performed under reaction conditions mild enough for use in polyfunctional or biologically significant systems. Comparably mild are methods involving photochemical[1d,5)] or electrochemical[6)] generation of trifluoromethyl radicals, or generation from trifluoroacetyl peroxide.[7)] These methods often yield isomer mixtures or, when regioselective, may give mainly undesired isomers. In order to provide better routes to specific isomers, we considered the introduction of reversible blocking groups on ring carbons prior to photochemical trifluoromethylation, and demonstrate here the utility of methylthio groups for this purpose. Such groups are introduced and removed with relative ease. In addition, the mildly electron-donating methylthio group would be expected to help reverse the deactivation of heteroaromatic rings by electronegative substituents,[5a)] and offers the further possibility of conversion to potentially bioactive sulfoxides and sulfones. In views of our particular interest in (perfluoroalkyl)imidazoles and pyrroles, these heteroaromatic systems received our first attention. In this study, the ring NH functions are blocked as *N*-methyl but other photostable protective groups, which are readily removed by acid hydrolysis or by hydrogenolysis, should be equally applicable. Furthermore, our previous results[5a)] have shown that trifluoromethylation is representative of perfluoroalkylation in general.

Results and Discussion

The methylthio group was introduced by selective deprotonations of **1a**[8)] and **1b**[9)] (Scheme 1) with butyllithium and reaction of the resulting carbanions with dimethyl disulfide. The use of an equivalent of butyllithium provided mono(methylthio) derivatives **2** in high yield. Two equivalents of butyllithium led to the bis(methylthio) derivatives **3** but, even in the presence of excess base or with **2** as the starting material, formation of **3** was never complete. Fortunately, **2** and **3** are readily separated by fractional vacuum distillation. In contrast to our results, **2a** (containing *N*-methoxymethyl in place of methyl) has been reported to undergo deprotonation at S–CH_3 rather than at a ring position.[10)] The preferential formation of the carbanion at C-2 in *N*-methylimidazole (**1a**)[11)] and in *N*-methylpyrrole (**1b**)[9,12)] is governed by the inductive effects of the ring nitrogen atoms. The generation of the second carbanion in **1a** occurs exclusively at C-5 and leads to the single bis(methylthio) product **3a**.[8)] This selectivity is determined by the strong repulsion that would exist between adjacent sp^2 lone pairs at N-3 and a C-4 carbanion (the ALP effect).[13)]

Photochemical trifluoromethylation was performed according to our published procedure,[5a)] samples being irradiated in quartz ampules for 7 d at ambient temperature. According to the solubility of the starting compound, either methanol or acetonitrile was used as solvent and triethylamine was added to neutralize the hydrogen iodide evolved. As seen from the results in Table 1, the choice of solvent has relatively little effect on yield or isomer distribution.

The photochemical trifluoromethylation of 1-methyl-2-(methylthio)imidazole (**2a**) gave mixtures of **4a** and **5a**, the latter being the major isomer (Table 1).[14)] A bis(trifluoromethyl) product was not observed. Several criteria were used to assign isomer structure: (a) coupling patterns of the ^{13}C NMR signal for C-4 and C-5 with CF_3 group;[15)] (b) the ^{19}F NMR signal for 4-CF_3 appears at higher field than for 5-CF_3;[5b)] (c) the ring proton in **5a** (meta-like) is found at higher field than that in **4a** (para-like);[16)] (d) weak coupling is observed between the N–CH_3 and the adjacent CF_3 group; (e) products were compared with authentic samples following reductive



Scheme 1.

Table 1. Yields and Conversions in Trifluoromethylation by UV Irradiation of 1-Methyl-2-methylthioimidazole (**2a**)

CF_3I (equiv)	Solvent	Yields[a]/%		
		4a	**5a**	**2a**
0.5	CH_3CN	0.8	11.9	31.2
0.5	CH_3OH	2.7	14.1	30.3
1.2	CH_3CN	1.5	25.0	12.7
1.2	CH_3OH	2.8	20.7	47.4
2.5	CH_3CN	2.6	29.3	0.7
2.5	CH_3OH	3.2	30.8	26.1

a) Isolated yields based on the imidazole, not adjusted for recovered **2a**.

Table 2. Yields and Conversions in Trifluoromethylation by UV Irradiation of 1-Methyl-2,5-bis(methylthio)imidazole (**3a**)

CF_3I (equiv)	Solvent	Yields[a]/%		
		5a[b]	**7a**[c]	**3a**[c]
0.5	CH_3CN	1.3	6.3	43.3
1.2	CH_3CN	2.9	7.8	32.0
1.2	CH_3OH	—	7.2	12.3
2.5	CH_3CN	2.3	8.3	31.1

a) Based on the imidazole, not adjusted for recovered **3a**. b) Determined by ^{19}F NMR. c) Isolated yields.

removal of the methylthio group. The direct trifluoromethylation of 1-methylimidazole had given three isomeric products (2-CF_3 : 4-CF_3 : 5-CF_3) in the ratio 43 : 8 : 50, separation requiring the use of both preparative gas and column chromatography.[5a] On the other hand, isomers **4a** and **5a** were formed in the ratio 10 : 90, the increased degree of substitution at C-5 probably being due to the electron-releasing effect of the methylthio group.

The 4-CF_3 isomer is the most difficult to obtain by photochemical trifluoromethylation of either **1a** or **2a**. Although C-4 is the only vacant ring position in **3a**, yields of **7a** never exceeded 6—8% (Table 2), even with 2.5 equiv of CF_3I. Interestingly, **7a** was accompanied by smaller amounts of **5a**, which may have arisen due to a slow photochemical conversion of **3a** to **2a**.

Photochemical trifluoromethylation of 1-methylpyrrole (**1b**) has been reported to yield the 2-trifluoromethyl derivative (**9b**) in 35% yield.[1d] We have confirmed this result, but found that excess CF_3I also provides a small yield (Table 3) of the 2,5-bis(trifluoromethyl) derivative (**10b**). Unfortunately, the boiling points of **9b** and **10b** are too close to permit clean separation and yields given in Table 3 are based on GC analysis. Although *N*-methylpyrrole undergoes efficient α-perfluoroalkylation with higher bis(perfluoroalkanoyl) peroxides, introduction of the CF_3 group could not be achieved.[7] The results of trifluoromethylation of **2b** are given in Table 4. Significant yields of **5b** require the use of at least 2.5 equiv of CF_3I, but small amounts of a bis(trifluoromethyl) derivative, presumably **6b**, are also formed. Fortunate-

Table 3. Yields in Trifluoromethylation by UV Irradiation of 1-Methylpyrrole (**1b**)

CF_3I (equiv)	Solvent	Yields[a]/%		
		9b	**10b**	**1b**
1.2	CH_3CN	36.5	—	10.5
2.5	CH_3CN	32.2	7.4	—

a) Determined by GC analysis based on the pyrrole, not adjusted for recovered **1b**.

Table 4. Yields and Conversions in Trifluoromethylation by UV Irradiation of 1-Methyl-2-methylthiopyrrole (**2b**)

CF_3I (equiv)	Solvent	Yields[a]/%		
		6b[b]	**5b**[c]	**2b**[c]
0.5	CH_3CN	—	4.2	18.4
1.2	CH_3CN	—	17.7	4.7
2.0	CH_3CN	0.14	18.8	5.0
2.5	CH_3CN	1.24	33.3	5.3

a) Based on the pyrrole, not adjusted for recovered **2b**. b) Determined by GC analysis. c) Isolated yields.

Table 5. Yields and Conversions in Trifluoromethylation by UV Irradiation of 1-Methyl-2,5-bis(methylthio)pyrrole (**3b**)

CF_3I (equiv)	Solvent	Yields[a]/%		
		5b[b]	**7b**[c]	**3b**[c]
0.5	CH_3CN	6.7	2.3	29.5
1.2	CH_3CN	10.2	3.9	38.1
2.5	CH_3CN	23.6	7.0	7.0

a) Based on the pyrrole, not adjusted for recovered **3b**. b) Determined by ^{19}F NMR. c) Isolated yields.

ly, the methylthio group facilitates the separation of mixtures by increasing boiling points and R_f differences in silica-gel chromatography.

Introduction of the trifluoromethyl group at the β-position of the pyrrole ring has not been achieved by direct or indirect methods. The reaction of 5-methyl-2-pyrrolecarbaldehyde with bis(heptafluorobutyryl) peroxide provided the 3-heptafluoropropyl derivative,[7] but this method failed to provide the trifluoromethyl derivative. Photochemical trifluoromethylation of **3b** provided the desired product **7b**. Even at a level of 2.5 equiv of CF_3I, the yield of **7b** was only 7% and was accompanied by 17% of **5b** (Table 5). Detection of a trace of **2b** suggested that the apparent replacement of the methylthio group by trifluoromethyl, both in the conversion of **3a** to **5a** and **3b** to **5b**, may actually be due to a prior loss of the methylthio group by irradiation. On the other hand, products devoid of the methylthio group were not detected in the photochemical trifluoromethylation of **2a** or **2b**.

Methylthio groups were removed by hydrogenolysis with Raney nickel in refluxing ethanol.[17] The imidazole derivatives provided the expected products in yields of 50—90%, and these products were readily isolated and purified by vacuum distillation in a microtube oven. In each case, properties of the sulfur-free imidazole coincided with those of authentic samples.[5a] On the other hand, the lower boiling points of (trifluoromethyl)pyrroles (and their closeness to that of ethanol) rendered isolation and purification difficult. Even the use of higher boiling alcohols as reaction solvents did not eliminate this problem. Thus, spectral properties were determined in mixtures containing some solvent. Yields were determined by GC analysis and were found comparable to those of the imidazoles. Reduction at 90—100 °C gave somewhat higher yields than at the temperature of refluxing ethanol. For certain (trifluoromethyl)pyrroles, therefore, it may be necessary to use the materials for further synthetic procedures without recovery of the pure product.

In these test cases, the overall yields of trifluoromethylated products were found to be comparable (or even inferior) to those obtained by direct photochemical trifluoromethylation. On the other hand, laborious isomer separations have been eliminated. Finally, this method provides a route to β-(trifluoromethyl)pyrroles, isomers which have not yet been obtained by direct trifluoromethylation.

Experimental

Analytical Methods and Instrumentation. All boiling and melting points are uncorrected. ^1H NMR spectra were measured on a Hitachi R-90H (90 MHz) instrument with tetramethylsilane as internal reference. ^{19}F NMR spectra were measured on a Hitachi R-90F (84.67 MHz) instrument with trifluoroacetic acid as external reference. Gas chromatographic analyses were performed on a Shimadzu GC-4A instrument (column KF-96, 3m). Mass spectra were obtained on a Hitachi M-80 instrument with 20 eV electron impact ionization.

Materials. Trifluoromethyl iodide was prepared by reaction of silver trifluoroacetate and iodine.[18] The following methylthio compounds were prepared according to literature methods: 1-methyl-2-(methylthio)imidazole, **2a**, 55% yield, bp 124—125 °C/30 Torr (1 Torr=133.322 Pa) (lit,[8] 65—70 °C/0.5 Torr); 1-methyl-2,5-bis(methylthio)imidazole, **3a**, 34% yield, bp 104—105 °C/5 Torr (lit,[8] 100—110 °C/0.5 Torr); 1-methyl-2-(methylthio)pyrrole, **2b**, 73% yield, bp 90—91 °C/30 Torr (lit,[9] 144—145 °C/12 Torr). Raney nickel (Aldrich) was used as a suspension in ethanol after thorough washing of the commercial material with water and ethanol.

2,5-Bis(methylthio)pyrrole (3b). To a solution of 2-(methylthio)pyrrole (**2b**, 2.77 g, 21.8 mmol) and *N,N,N',N'*-tetramethylethylenediamine (3.33 g, 28.7 mmol) in hexane (20 mL), was added dropwise a hexane solution of butyllithium (1.6 M, 18 mL, 1.2 equiv) at 30 °C under nitrogen. The reaction mixture became dark red instantly, and the suspension was stirred for 1 h. To the reaction mixture, cooled in an ice bath, was added dimethyl disulfide (2.70 g, 28.7 mmol) in hexane (5 mL). The reaction mixture was stirred at 0 °C for 1 h, and was then poured into water (50 mL). The organic layer was separated, washed with water and dried ($MgSO_4$). The water

layer was extracted with ethyl acetate (2×100 mL) and the organic layer was treated in a similar manner. Vacuum distillation of the combined organic layers afforded 2,5-bis(methylthio)pyrrole (**3b**, 1.58 g, 31.8% yield) as a colorless oil, bp 94—95 °C/7 Torr; ^{1}H NMR ($CDCl_3$) δ=2.26 (s, 6H, SCH_3), 3.72 (s, 3H, NCH_3), 6.30 (s, 2H, ring); MS *m/z* 173 (M^+ 100%), 158 (84), 117 (70). Found: C, 48.78; H, 6.23; N, 8.35%. Calcd for $C_7H_{11}NS_2$: C, 48.52; H, 6.40; N, 8.08%.

UV-Induced Trifluoromethylation of 1-Methyl-2-(methylthio)imidazole (2a). Into a solution of **2a** (2.56 g, 20.0 mmol) and triethylamine (2.43 g, 24.0 mmol) in acetonitrile (10 mL), was bubbled gaseous trifluoromethyl iodide until the weight had increased by 4.70 g (24.0 mmol). The solution was placed in a quartz tube and the remaining upper space was filled with argon. The tube was sealed with a glass stopper and then the solution was irradiated for 7 d at ambient temperature, using a 60 W low-pressure mercury lamp equipped with a Vycor filter.

The dark orange reaction mixture was poured into water and the products were extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The residual oil was subjected to silica-gel chromatography with CH_2Cl_2 and ether as successive eluents to provide, in order, **4a** (1.5%), **5a** (25.0%), and **2a** (12.7%). The eluting solvent was removed and the product purified by vacuum distillation using a glass tube oven. Additional runs are summarized in Table 1.[19]

1-Methyl-2-methylthio-4-(trifluoromethyl)imidazole (4a): White needles, mp 44—46 °C; ^{1}H NMR (acetone-d_6) δ=26.0 (s, 3H, SCH_3), 3.66 (br s, 3H, NCH_3), 7.63 (q, 1H, *J*=1.1 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ_C=15.8 (s, SCH_3), 33.3 (s, NCH_3), 121.7 (q, *J*=267 Hz, CF_3), 121.8 (q, *J*=4.1 Hz, C-5), 131.9 (q, *J*=39 Hz, C-4), 145.8 (s, C-2); ^{19}F NMR (acetone-d_6) δ_F=14.8 (s); MS *m/z* 196 (M^+ 100%), 163 (54) Found: C, 36.65; H, 3.57; N, 14.40%. Calcd for $C_6H_7N_2F_3S$: C, 36.73; H, 3.60; N, 14.28%.

1-Methyl-2-methylthio-5-(trifluoromethyl)imidazole (5a): Colorless oil, bp 98—99 °C/30 Torr; ^{1}H NMR (acetone-d_6) δ=2.64 (s, 3H, SCH_3) 3.65 (br s, 3H, NCH_3), 7.42 (q, *J*=1.5 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ_C=15.3 (s, SCH_3), 31.6 (d, *J*=1.4 Hz, NCH_3), 121.0 (q, *J*=266 Hz, CF_3), 123.2 (q, *J*=39 Hz, C-5), 130.9 (q, *J*=4.2 Hz, C-4), 149.1 (br s, C-2); ^{19}F NMR (acetone-d_6) δ_F=17.3 (s); MS *m/z* 196 (M^+ 100%), 163 (59). Found: C, 36.30; H, 3.68; N, 14.77%. Calcd for $C_6H_7N_2F_3S$: C, 36.73; H, 3.60; N, 14.28%.

UV-Induced Trifluoromethylation of 1-Methyl-2,5-bis(methylthio)imidazole (3a). Trifluoromethylation of **3a**, by the procedure described above, gave **7a** (7.8%), **5a** (2.9%), and unreacted **3a** (32.0%). The mixture of imidazoles was separated by silica-gel chromatography with 50% hexane/50% CH_2Cl_2 and 100% CH_2Cl_2 as successive eluents and products were eluted in the order given. Additional runs are summarized in Table 2.

1-Methyl-2,5-bis(methylthio)-4-(trifluoromethyl)imidazole (7a): White needles, mp 39—40 °C; ^{1}H NMR (acetone-d_6) δ=2.33 (s, 3H, SCH_3), 2.63 (s, 3H, SCH_3), 3.65 (br s, 3H, NCH_3); ^{19}F NMR (acetone-d_6) δ_F=16.6 (s); MS *m/z* 242 (M^+ 100%), 227 (46), 209 (45), 186 (37). Found: C,34.38; H, 3.77; N, 11.52%. Calcd for $C_7H_9N_2F_3S_2$: C, 34.70; H, 3.74; N, 11.56%.

UV-Induced Trifluoromethylation of 1-Methylpyrrole (1b). Following the procedure used with **2a**, **1b** gave **9b** and **10b** or **9b** and recovered **1b**. The results are given in Table 3. It was difficult to separate **9b**, **10b**, and **1b** because the boiling points are very close to one another, therefore, these materials were identified in a mixture and the yields are based on GC analysis.

1-Methyl-2-(trifluoromethyl)pyrrole (9b): ^{1}H NMR (acetone-d_6) δ=3.73 (s, 3H, SCH_3), 6.07 (m, 1H, ring), 6.53 (m, 1H, ring), 6.88 (m, 1H, ring); ^{19}F NMR (acetone-d_6) δ_F=18.6 (s); MS *m/z* 149 (M^+ 100%), 130 (36).

1-Methyl-2,5-bis(trifluoromethyl)pyrrole (10b): ^{1}H NMR (acetone-d_6) δ=3.83 (s, 3H, SCH_3), 6.66 (s, 2H, ring); ^{19}F NMR (acetone-d_6) δ_F=17.6 (s); MS *m/z* 217 (M^+ 100%), 198 (40), 156 (21).

UV-Induced Trifluoromethylation of 1-Methyl-2-(methylthio)pyrrole (2b). Following the procedure used with **2a**, **2b** gave **5b** (17.7%) and **2b** (4.7%). The mixture of pyrroles was separated by silica-gel chromatography with 90% hexane/10% CH_2Cl_2 and 100% CH_2Cl_2 as successive eluents. The results of additional runs are given in Table 4. At higher ratios of CF_3I, small amounts of a bis(trifluoromethyl)derivative, probably **6a**, were also obtained. The material was identified by mass spectrum (M^+ 263) and yields are based on GC analysis; however, no effort was made to isolate **6b**.

1-Methyl-2-methylthio-5-(trifluoromethyl)pyrrole (5b): Colorless oil, bp 80—81 °C/30 Torr; ^{1}H NMR (acetone-d_6) δ=2.32 (s, 3H, SCH_3), 3.77 (q, 3H, *J*=0.7 Hz, NCH_3), 6.31 (AB, 1H, *J*=4.0 Hz, H-3), 6.57 (AB-q, 1H, *J*=4.0 Hz and 0.9 Hz, H-4); ^{19}F NMR δ_F=17.9 (s); MS *m/z* 195 (M^+ 100%), 180 (61). Found: C, 43.02; H, 4.17; N, 7.09; S, 16.36%. Calcd for $C_7H_9NF_3S$: C, 43.07; H, 4.13; N, 7.18; S, 16.42%.

UV-Induced Trifluoromethylation of 1-Methyl-2,5-bis(methylthio)pyrrole (3b). Following the procedure used with **2a**, **3b** gave **7b** (3.9%), **5b** (10.2%), and unreacted **3b** (38.1%). The mixture of pyrroles was separated by silica-gel chromatography with 100% hexane; the pure products were obtained following removal of solvent in a glass tube oven. The results of additional runs are given in Table 5.

1-Methyl-2,5-bis(methylthio)-3-trifluoromethylpyrrole (7b): Colorless oil, bp 164—168 °C; ^{1}H NMR (acetone-d_6) δ=2.29 (s, 3H, SCH_3), 2.36 (s, 3H, SCH_3), 3.83 (br s, 3H, NCH_3), 6.56 (br s, 1H, H-4); ^{19}F NMR (acetone-d_6) δ_F=20.9 (s); MS *m/z* 241 (M^+ 100%), 226 (73) 185 (74). Found: C, 39.88; H, 4.21; N, 5.72%. Calcd for $C_7H_9N_2F_3S_2$: C, 39.82; H, 4.18; N, 5.80%.

Hydrogenolysis of Methylthio Groups of Imidazoles. To an ethanol solution (30 mL) of 1-methyl-2-methylthio-5-(trifluoromethyl)imidazole (**5a**) (1.34 g, 6.81 mmol) was added Raney nickel dampened with ethanol (ca. 10 g), and the reaction mixture was vigorously stirred under reflux for 5 h. The nickel was removed by filtration, the filtrate was poured into water (100 mL) and the mixture was extracted with dichloromethane (3×100 mL). The combined organic layers were washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue was vacuum distilled in a glass tube oven to give **9a** in 57.3% yield.

1-Methyl-5-(trifluoromethyl)imidazole (7a): White needles, mp 38—41 °C; ^{1}H NMR (acetone-d_6) δ=3.83 (s, 3H, NCH_3), 7.41 (br s, 1H, H-4), 7.76 (br s, 1H, H-2) (lit,[5a] δ=3.83, 7.40, 7.75); ^{19}F NMR δ_F=17.8 (s); MS *m/z* 150 (M^+).

Hydrogenolysis of methylthio groups in other imidazoles was carried out by a similar procedure.

1-Methyl-4-(trifluoromethyl)imidazole (8a): 54.5% yield from **4a**, 86.6% yield from **7a**; colorless oil, bp 222—225 °C; ^{1}H NMR (acetone-d_6) δ=3.82 (br s, 3H, NCH_3), 7.58 (br s, 1H, H-2), 7.66 (br s, 1H, H-5) (lit,[5a] δ=3.88, 7.58, 7.64); ^{19}F NMR

δ_F=15.3 (s); MS *m/z* 150 (M^+).

Hydrogenolysis of Methylthio Groups in Pyrroles. To an ethanol solution (25 mL) of 1-methyl-2-methylthio-5-(trifluoromethyl)pyrrole (**5b**) (1.68 g, 8.60 mmol), was added Raney nickel dampened with ethanol (ca. 15 g), and the reaction mixture was vigorously stirred under reflux for 1 h. The nickel was removed by filtration, the filtrate was poured into water (100 mL), and the mixture was extrated with dichloromethane (2×100 mL). The organic layers were combined, washed with water and dried (Na_2SO_4). The solvent was removed and the estimated yield of **9b** was 60%, determined by GC analysis. Properties of **9b** were determined using a sample (90% purity) obtained in a microdistillation apparatus.

1-Methyl-2-(trifluoromethyl)pyrrole (9b): Colorless oil, bp. 114 °C; ^{1}H NMR (acetone-d_6) δ=3.75 (br s, 3H, NCH_3), 6.08 (m, 1H, ring) 6.55 (m, 1H, ring), 6.91 (m, 1H, ring) (lit,[1d] ($CDCl_3$) δ=3.60, 5.90, 6.36, 6.48); ^{19}F NMR δ_F=18.8 (s); MS *m/z* 149 (M^+).

Hydrogenolysis of the methylthio groups of **7b** was carried out by a similar procedure, and the estimated yield of **8b** was 41% determined by GC analysis. A sample of **8b** could not be obtained by preparative GC and microdistillation led to a dark tarry product; properties of **8b** were determined using a dichloromethane solution.

1-Methyl-3-(trifluoromethyl)pyrrole (8b): ^{19}F NMR (acetone-d_6) δ_F=21.0 (s); *m/z* 149 (M^+).

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