8.12 (s, 1 H, CH=N); 8.20 (d, 2 H arom.); 8.37 (NH_2); 11.7 (s, 1 H, N=NH). ^{13}C NMR, δ: 123.6 (CH–C–NO_2); 128.0 (CH–C–CH=N); 139.5 (CH=N); 140.6 (C–CH=N); 147.5 (C–NO_2); 178.6 (C=S). MS, *m/z*: $[M]^+$ 224.

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Comparison of α- and β-trifluoromethylsubstituted acrylic acids in their reactions with thiols

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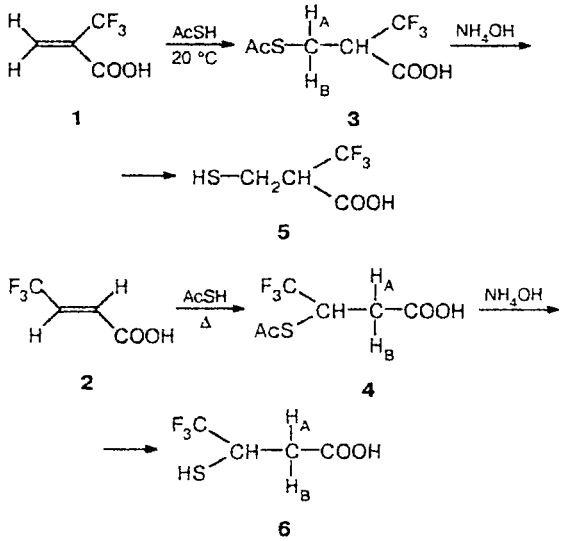
α-(Trifluoromethyl)acrylic acid (**1**) and γ,γ,γ-trifluorocrotonic acid (**2**) add AcSH (exothermally and at 100 °C, respectively) in the absence of a catalyst to form products of β-thiolation, which can be easily hydrolyzed to the corresponding β-mercaptoalkanoic acids. Thiols also add regiospecifically to acids **1** (in the absence of a catalyst) and **2** (only in the presence of trifluoromethanesulfonic acid as the catalyst) when heated.

Key words: α-(trifluoromethyl)acrylic acid, γ,γ,γ-trifluorocrotonic acid, thiolacetic acid; thiols, thiolation.

There are few reports on the addition of nucleophiles to the C=C bond of α-(trifluoromethyl)acrylic (**1**) and γ,γ,γ-trifluorocrotonic (**2**) acids. In the presence of enzymes, acid **1** reacts with water, diethylamine, and thiophenol and does not react with ethanol or phenol.[1,2] Addition of ammonia to acid **2** occurs under drastic conditions.[3] The reactions of compounds **1** and **2** with thiols and thiolcarboxylic acids were not studied. Acid **1** was found to react exothermally with AcSH to form only the product of β-thiolation (**3**). Acid **2** reacts regiospecifically with AcSH to give the β-(acetylthio) derivative **4**, but only when heated. The presence of air oxygen does not affect the direction of these reactions. The synthesized β-(acetylthio)substituted acids **3** and **4** were converted to β-mercaptoacids **5** and **6** by treating them with aqueous ammonia (Scheme 1).

The addition of thiols to acids **1** and **2** is much more difficult. For example, the reaction of acid **1** with α-toluenethiol occurs at a reasonable rate only at 100 °C to give exclusively benzyl sulfide **7** in a high yield. Under these conditions, acid **2** does not form any addi-

Scheme 1



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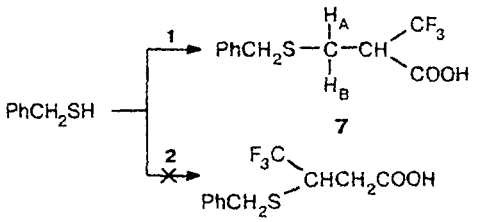
tion product even after prolonged heating (more than 10 h) (Scheme 2).

Scheme 2



The reactions of thiols with acid **2** occur under drastic conditions even in the presence of acid catalysts. For example, the addition of *n*-pentanethiol in the presence of trifluoromethanesulfonic acid occurs at an appreciable rate only at 120 °C. The fact that thioester **9** is formed in addition to the product of β-thiolation **8** is unusual (Scheme 3).

Scheme 3

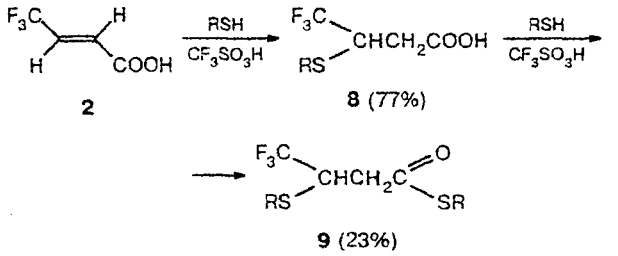


Table 1. Physicochemical and spectral characteristics of compounds **3**—**7**

Compound	Yield (%)	B.p./°C (*p*/Torr) [M.p./°C]	n_D (*T*/°C)	Found / Calculated (%) C	H	F[S]	Molecular formula	δ ^{19}F (*J*/Hz)	δ ^{1}H (*J*/Hz)	ν/cm^{-1}
3	87	95—98 (3)	1.4380 (18)	33.24 / 33.33	3.30 / 3.24	26.47 / 26.39	$C_6H_7F_3O_3S$	−9.84 (d, CF_3, J = 7.5)	2.36 (s, Ac); 3.10—3.35 (m, H_A); 3.35—3.58 (m, H_B + CH); 10.93 (s, COOH)	1730—1755 (AcS, COOH); 2800—3400 (OH); 1140, 1170 (C—F)
4	90	115—122 (3) [83—85]	—	33.20 / 33.33	3.03 / 3.24	[14.90] / [14.81]	$C_6H_7F_3O_3S$	−6.71 (d, CF_3, J = 7.6)	2.39 (s, Ac); 2.71 (dd, H_A, J = 16.5, 9.1); 3.03 (dd, H_B, J = 16.5, 4.6); 4.6 (oct., CH); 10.36 (s, COOH)	1730—1752 (AcS, COOH); 2850—3200 (OH); 1135, 1160 (C—F)
5	52	66—66.5 (2—3)	1.4170 (18)	27.52 / 27.59	2.66 / 2.87	32.59 / 32.76	$C_4H_5F_3O_2S$	−10.07 (d, CF_3, J = 7.5)	1.75 (t, SH, J = 8.3); 2.82—3.52 (m, CH_2CH); 11.24 (s, COOH)	1745 (COOH); 2600—2690 (SH); 2900—3300 (OH); 1130, 1180 (C—F)
6	81	73—76 (2—3) [33—35]	1.4128 (24)	27.63 / 27.59	3.17 / 2.87	32.73 / 32.76	$C_4H_5F_3O_2S$	−4.36 (d, CF_3, J = 8.0)	2.07 (d, SH, J = 8.55); 2.61 (dd, H_A, J = 15.2, 9.5); 3.05 (dd, H_B, J = 15.2, 3.8); 3.68 (m, CH); 10.93 (s, COOH)	1714 (COOH); 2565, 2662 (SH); 2800—3200 (OH); 1113, 1162 (C—F)
7	79	[47—48] (hexane)*	—	50.00 / 50.00	4.33 / 4.17	[12.02] / [12.12]	$C_{11}H_{11}F_3O_2S$	−9.19 (d, CF_3, J = 9.0)	2.69 (dd, H_A, J = 14.0, 4.0); 2.84 (dd, H_B, J = 14.0, 10.5); 3.12 (n.m, CH); 3.69 (s, CH_2Ph); 11.3 (s, COOH); 7.19 (s, C_6H_5)	1740—1750 (COOH); 2900—3200 (OH); 1120, 1170 (C—F)

* Solvent for crystallization.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker WP-200SY spectrometer (200.12 and 188.31 MHz, respectively) in $CDCl_3$; HMDS and CF_3COOH were used as the internal and external standards. IR spectra were recorded on an UR-20 spectrophotometer in KBr tablets or in a thin layer without solvent. Mass spectra were measured on a VG-7070E spectrometer (EI, 70 eV). Physicochemical and spectral characteristics and the elemental analysis data of compounds **3**—**7** are presented in Table 1.

3-Acetylthio-2-trifluoromethylpropionic acid (3). AcSH (1.14 g, 15 mmol) was added to acid **1** (1.5 g, 10.7 mmol). After completion of the exothermal reaction, the reaction mixture was allowed to stand at 20 °C for 1.5 h. Product **3** was isolated by distillation.

3-Acetylthio-4,4,4-trifluorobutyric acid (4). A mixture of acid **2** (7.5 g, 54 mmol) and AcSH (5.7 g, 75 mmol) was refluxed at 96—97 °C for 4 h, until the reaction was complete (TLC monitoring). Product **4** was then isolated by distillation.

3-Mercapto-2-trifluoromethylpropionic acid (5). Acid **3** (1.7 g, 7.9 mmol) was added to a mixture of conc. NH_4OH (4.5 mL) and water (4.5 mL) under argon with stirring. When the slightly exothermal reaction ceased, the mixture was stirred at 20 °C for 50 min and poured into dilute HCl. The product was extracted with diethyl ether and dried over Na_2SO_4. Subsequent distillation gave acid **5**.

3-Mercapto-4,4,4-trifluorobutyric acid (6). Acid **6** (3.27 g) was obtained similarly from acid **4** (5 g, 23 mmol) as an oil that crystallized on cooling,.

3-Benzylthio-2-trifluoromethylpropionic acid (7). A mixture of acid **1** (1 g, 7 mmol) and α-toluenethiol (0.97 g, 7.86 mmol) was heated in a closed vessel under argon at 100 °C until the reaction was complete (1.5 h). The next day the precipitate that had formed was filtered off, washed with hexane, and crystallized from hexane to afford product **7**.

Interaction of acid 2 with *n*-pentanethiol. A mixture of acid **2** (1 g, 7 mmol), n-$C_5H_{11}SH$ (1.11 g, 10 mmol), and CF_3SO_3H (0.11 g, 0.7 mmol) was heated at 120 °C for 17 h. The reaction mixture was dissolved in $CHCl_3$, washed with water, and dried over Na_2SO_4. Distillation gave the adduct (1.58 g), b.p. 105—111 °C (3 Torr) as colorless low-melting crystals. The distillate contained 77% acid **8** and 23% thioester **9** (according to TLC (silica gel, ether—hexane, 1 : 2), the mass-, ^1H and ^{19}F NMR and IR spectra, the elemental analysis data (C, H, F), and results of titration with NaOH).

IR, ν/cm^{-1}: **8**, 1700; **9**, 1735. ^{19}F NMR, δ: **8**, −6.33 (d, CF_3, J = 7.9 Hz); **9**, −6.59 (d, CF_3, J = 9.5 Hz). ^1H NMR, δ: **8** + **9**, 0.88 (t, CH_3, J = 6.3 Hz); 1.25—1.62 (m, $(CH_2)_3$); 2.45—2.98 (m, CH_2CO + CH_2S); **8**, 10.9 (s, COOH). MS, m/z (I_{rel} (%)): **8**, 244 $[M]^+$ (19.4); 224 $[M-HF]^+$ (12.9); 157 $[M-CF_3-H_2O]^+$ (23.7); 103 $[C_5H_{11}S]^+$ (100); 70 $[CHF_3]^+$ (58.1); 69 $[CF_3]^+$ (58.1); 55 $[C_4H_7]^+$ (40.9); 43 $[C_3H_7]^+$ (63.4); 42 $[C_3H_6]^+$ (63.4); **9**, 330 $[M]^+$ (8.6); 259 $[M-C_5H_{11}]^+$ (6.5); 227 $[M-C_5H_{11}S]^+$ (15.1); 226 $[M-C_5H_{12}S]^+$ (24.7); 199 $[M-COSC_5H_{11}]^+$ (40.9); 103 $[C_5H_{11}S]^+$ (17.2); 71 $[C_5H_{11}]^+$ (62.4); 69 $[CF_3]^+$ (18.3); 43 $[C_3H_7]^+$ (100).

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