2-(2,2,2-Trifluoroethylidene)-1,3-dithianes. New Intermediates for the Preparation of CF_3-Containing Compounds

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A simple and efficient synthesis of 2-(2,2,2-trifluoroethylidene)-1,3-dithianes is described. The title compounds are versatile intermediates for the preparation of trifluoromethyl derivatives.

A number of biologically active molecules contain a CF_3 group,[1] and hence there has been much interest in the preparation of simple building blocks containing the trifluoromethyl group.[2] Trifluoroacetic acid (TFA) and many derivatives thereof are commercially available, relatively inexpensive, and therefore suitable starting materials. Higher homologues are less accessible although they are well known.[2,3] We describe herein a method for the preparation of 2-(2,2,2-trifluoroethylidene)-1,3-dithianes which are useful intermediates for the synthesis of trifluoromethyl-containing molecules. TFA anhydride was first selected as a low-cost CF_3-containing starting material. From its reaction with two equivalents of 2-lithio-1,3-dithiane at − 78 °C, however, a near 1:1 mixture of the ketone **1** and the tertiary alcohol **5** together with recovered 1,3-dithiane was obtained. Variation in temperature and amount of nucleophile did not significantly improve the relative yield of the ketone **1**. When the electrophile was ethyl trifluoroacetate the yield of the ketone **1** was increased to 80 % when the reaction was run at −15 °C for 5 h. Under these conditions, the tertiary alcohol **5** amounted to only 2 % (GLC) of the crude product. This finding indicates that the addition of 2-lithio-1,3-dithiane to the carbonyl group is kinetically favoured over the deprotonation of the ketone **1** by 2-lithio-1,3-dithiane acting as a base. The lithium ethanolate from the ketone formation, however, may be the base which protects the ketone **1** from further addition by converting it to the enolate.

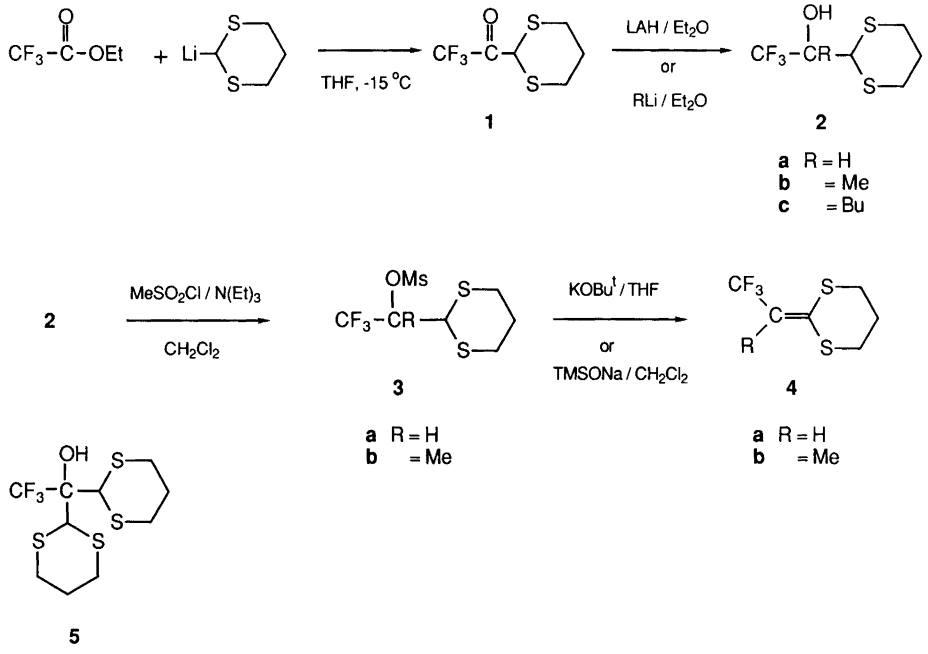
In the reactions of the ketone **1** with organometallics, lithium dimethylcuprate was tried initially because of its relatively low basicity, since the H-2 proton in the dithiane ring of the ketone was expected to be highly acidic. Organocopper compounds, however, are known to react slowly with ketones.[4] At best, dimethylcuprate gave a mixture of the starting material and the addition product **2b** in the ratio 2:3. The use of 1.1 mole equivalents of methyllithium, however, at −78 °C gave the tertiary alcohol **2b** in 79 % yield. BuLi reacted in the same manner (71 % yield). In contrast *sec*-BuLi and PhMgBr gave the corresponding alcohols in low yields (<10 %). With *sec*-BuLi the main product was due to the competitive β-hydrogen elimination and reduction to the alcohol **2a**.[5] Presumably the bulkiness of the dithiane ring hinders the approach to the carbonyl carbon and hence the reaction is sensitive to steric effects in the nucleophile. Steric interference is further demonstrated in mesylation reactions. The alcohols **2a** and **2b** (R = H, Me) are readily mesylated, whereas the butyl homologue **2c** underwent very little mesylation and the very bulky alcohol **5** did not react at all. Methanesulfonate can be eliminated from **2a** and **2b** by potassium *tert*-butoxide in THF or by sodium trimethylsilanolate in dichloromethane,[6] the products being the 2-(2,2,2-trifluoroethylidene)-1,3-dithianes **4**.

Cleavage of the ketene dithioacetals **4a** and **4b** with $HgO–H_2SO_4$ gives the corresponding acids **6**, and we therefore have a convenient and efficient synthesis of these important acids.[2g,3g,7] The double bond in the ketene dithioacetals **4** can be reduced by addition of sodium borohydride pellets to a solution in trifluoroacetic acid,[8] or with triethylsilane in trifluoroacetic acid.[9] The cleavage of the dithioacetal **7** with Hg(II) was run in ethanol whereby the acetals **8** were formed.

Acylation of the 2-(2,2,2-trifluoroethylidene)-1,3-dithiane **4a** under Friedel–Crafts conditions (acetyl chloride under the influence of zinc chloride catalysis) gives the α-oxoketene dithioacetal **9**; α-oxoketene dithioacetals are versatile intermediates in organic synthesis.[10]

Experimental

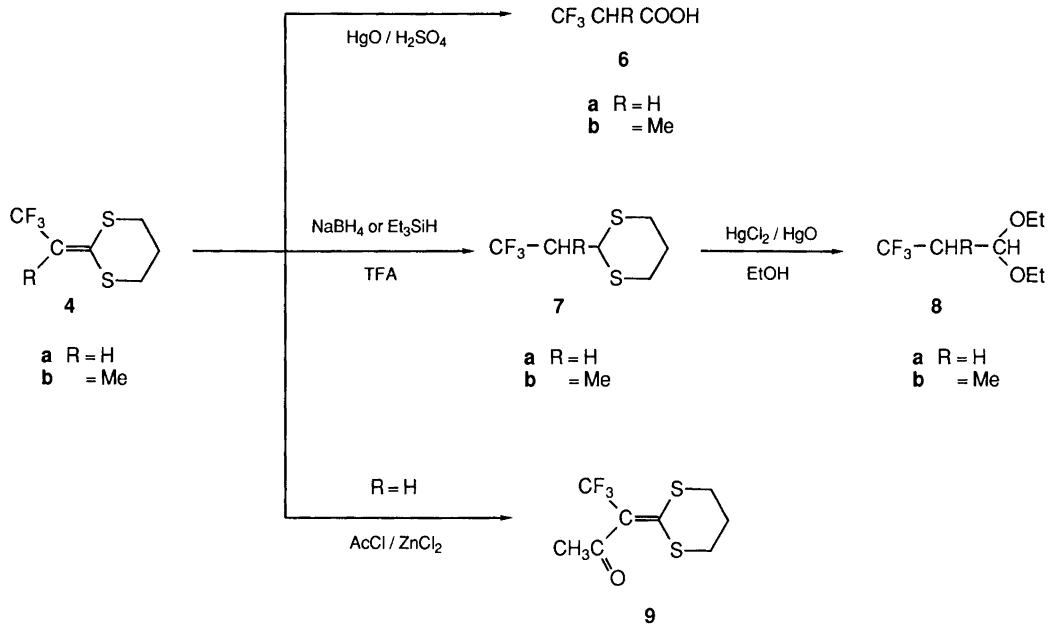
The ^1H NMR spectra were recorded at 60 MHz or at 300 MHz (specified). The mass spectra under electron-impact conditions were recorded at 70 eV ionizing voltage. Isobutane or ammonia was used for chemical ionization (CI).



Scheme 1.

2-(Trifluoroacetyl)-1,3-dithiane (**1**). A solution of butyllithium in hexane (1.5 M, 91.49 mmol) was added dropwise with stirring, under nitrogen, to a solution of 1,3-dithiane (10.00 g, 83.17 mmol) in dry THF (300 ml) at −78 °C. The mixture was stirred at −78 °C for 3 h, allowed to warm to 0 °C over 30 min, and cooled to −20 °C before ethyl trifluoroacetate (10.63 g, 74.85 mmol) was added. The temperature was kept between −15 and −10 °C for 5 h before water (150 ml) was added and the mixture neutralized with 3 M HCl. Most of the THF was removed on a rotary evaporator and the remaining mixture was extracted with diethyl ether and dried ($MgSO_4$). Concentration and distillation of the extract gave 12.99 g (80 %) of the title product, b.p. 54 °C/1.0 mmHg. Anal. $C_6H_7F_3OS_2$: C,H. ^1H NMR ($CDCl_3$): δ 1.7–3.9 (6 H, m), 4.52 (1 H, s). MS: 216 (6, *M*), 121 (10), 120 (9), 119 (100), 106 (2), 105 (2), 104 (2), 91 (7). IR (cm^{-1}, film): 1670 (C=O).

2-(2,2,2-Trifluoro-1-hydroxyethyl)-1,3-dithiane (**2a**). 2-(Trifluoroacetyl)-1,3-dithiane (30.00 g, 0.139 mol) in diethyl ether (50 ml) was added to a suspension of lithium aluminium hydride (5.80 g, 0.153 mol) in diethyl ether (200 ml) at



Scheme 2.

0 °C. After 15 min at ambient temperature the reaction mixture was refluxed for 90 min. The cooled mixture was poured into ice-water (150 ml), neutralized with 3 M hydrochloric acid and extracted with diethyl ether (3 × 100 ml). The dried ($MgSO_4$) solution was concentrated and distilled to give 26.34 g (87 %) of the product **2a**, b.p. 75 °C/0.2 mmHg. Anal. $C_6H_9F_3OS_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.8 – 2.3 (2 H, m), 2.7 – 3.1 (4 H, m), 3.43 (1 H, d, *J* 6 Hz), 4.1 – 4.5 (1 H m), 4.25 (1 H, s). MS: 218 (12, *M*), 153 (1), 149 (3), 121 (11), 120 (5), 119 (100).

2-(2,2,2-Trifluoro-1-hydroxy-1-methylethyl)-1,3-dithiane (**2b**). A solution of methyllithium in diethyl ether (2.0 M, 30.52 mmol) was added dropwise with stirring, under nitrogen, to a solution of 2-(trifluoroacetyl)-1,3-dithiane (6.00 g, 27.75 mmol) in dry diethyl ether (100 ml) at −78 °C. The mixture was stirred at −78 °C for 3 h and allowed to warm to ambient temperature over 30 min. The reaction mixture was poured into ice-cold hydrochloric acid (0.5 M, 100 ml) and the layers separated. The aqueous layer was extracted with diethyl ether (3 × 50 ml) and the combined ether extracts were dried ($MgSO_4$). Concentration and distillation of the extracts gave 5.12 g (79 %) of **2b** b.p. 62–64 °C/0.1 mmHg. Anal. $C_7H_{11}F_3S_2$: C, H. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (3 H, q, *J* 1.1 Hz), 1.8–2.0 (1 H, m), 2.1–2.2 (1 H, m), 2.85–3.0 (5 H, m), 4.41 (1 H, s). MS: 232 (2, *M*), 163 (1), 121 (11), 120 (6), 119 (100), 113 (2), 91 (6), 85 (6), 75 (12).

2-(1-Butyl-2,2,2-trifluoro-1-hydroxyethyl)-1,3-dithiane (**2c**). A solution of butyllithium in hexane (1.4 M, 40.69 mmol) was added dropwise with stirring, under nitrogen, to a solution of 2-(trifluoroacetyl)-1,3-dithiane (8.00 g, 36.99 mmol) in dry diethyl ether (150 ml) at −78 °C. After 13 h at −78 °C, the reaction mixture was allowed to warm to 0 °C and kept at this temperature for 2 h. The reaction mixture was worked up as for **2b** to give 7.05 g (71 %) of the product **2c**, b.p. 90–92 °C/0.01 mmHg. Anal. $C_{10}H_{17}F_3OS_2$: C, H. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (3 H, t, *J* 7.2 Hz), 1.3–1.5 (4 H, m), 1.85–2.0 (3 H, m) 2.1–2.2 (1 H, m), 2.85–3.0 (4 H, m), 3.09 (1 H, s, br), 4.39 (1 H, s). MS: (CI-isobutane): 275 (100, *M*+1), 274 (3), 257 (18), 119 (39).

2,2,2-Trifluoro-1-(1,3-dithian-2-yl)ethyl methanesulfonate (**3a**). Methanesulfonyl chloride (7.86 ml, 0.101 mol) was added to a solution of 2-(2,2,2-trifluoro-1-hydroxyethyl)-1,3-dithiane **2a** (20.00 g, 91.63 mmol) and triethylamine (19.12 ml, 0.138 mol) in dichloromethane (400 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min before the solution was washed consecutively with ice–water, 1 M hydrochloric acid, saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride. Drying ($MgSO_4$) and evaporation gave 26.61 g (98 %) of an analytically pure product **3a**, m.p. 53 °C. Anal. $C_7H_{11}F_3O_3S_3$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.9–2.2 (2 H, m), 2.7–3.1 (4 H, m), 3.24 (3 H, s), 4.17 (1 H, d, *J* 6 Hz), 5.22 [1 H, quint. (deg. dq), *J* 6 Hz]. MS: 296 (5, *M*), 202 (3), 201 (4), 200 (36), 121 (9), 120 (6), 119 (100).

2,2,2-Trifluoro-1-methyl-1-(1,3-dithian-2-yl)ethyl methanesulfonate (**3b**). Methanesulfonyl chloride (0.50 ml, 6.46 mmol) was added to a solution of 2-(2,2,2-trifluoro-1-hydroxy-1-methylethyl)-1,3-dithiane **2b** (1.00 g, 4.30 mmol) and triethylamine (1.19 ml, 8.60 mmol) in dichloromethane (20 ml) at 0 °C. The mixture was stirred at 0 °C for 30 min before it was worked up as for **3a** above to give 1.28 g (96 %) of a crystalline product, pure enough for further use, m.p. 79 °C (hexane). Anal. $C_8H_{12}F_3O_3S$: C,H. ^{1}H NMR ($CDCl_3$): δ 1.7–2.3 (2 H, m), 2.02 (3 H, s), 2.8–3.1 (4 H, m), 3.18 (3 H, s), 4.79 (1 H, s). MS: 310 (3, *M*), 217 (1), 216 (5), 215 (8), 214 (23), 121 (11), 120 (7), 119 (100).

2-(2,2,2-Trifluoroethylidene)-1,3-dithiane (**4a**): *Method A.* Potassium *tert*-butoxide (8.03 g, 71.56 mmol) was added to a solution of the methanesulfonate **3a** (17.30 g, 58.38 mmol) in THF (200 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and at 20 °C for 45 min before it was poured into ice–water (200 ml). Most of the THF was removed on a rotary evaporator and the remaining mixture was extracted with diethyl ether (3 × 100 ml) and dried ($MgSO_4$). Concentration and distillation of the extract gave 9.50 g (81 %) product, b.p. 44–46 °C/0.1 mmHg. Anal. $C_6H_7F_3S_2$: C, H. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 [2 H, quint. (deg. tt), *J* 6.8 Hz], 2.95–3.0 (4 H, m), 5.82 (1 H, q, *J* 8.2 Hz). MS: 200 (25, *M*), 181 (6), 167 (4), 149 (4), 147 (8), 138 (6), 126 (25), 45 (100).

Method B. Sodium trimethylsilanolate (0.448 g, 4.31 mmol) was added to a solution of the methanesulfonate **3a** (1.16 g, 3.91 mmol) in dichloromethane (20 ml) at 0 °C. The mixture was stirred at 0 °C for 15 min and at 20 °C for 45 min, before the mixture was washed with saturated aqueous sodium hydrogen carbonate (10 ml) and saturated aqueous sodium chloride (3 × 10 ml). After being dried ($MgSO_4$) and concentrated, the product was purified by Kugelrohr distillation (85 °C, 1.2 mmHg). Yield, 0.60 g (77 %).

2-(2,2,2-Trifluoro-1-methylethylidene)-1,3-dithiane (**4b**): *Method A.* Compound **4b** was obtained from the methanesulfonate **3b** using method A above. The crude product was purified by Kugelrohr distillation (70 °C/1.1 mmHg). Yield 75 %. Anal. $C_7H_9F_3S_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.94 (3 H, s), 1.9–2.3 (2 H, m), 2.8–3.2 (4 H, m). MS: 214 (100, *M*), 213 (14), 195 (7), 181 (4), 172 (10), 145 (20), 140 (30), 139 (49).

Method B. Sodium trimethylsilanolate (2.49 g, 22.20 mmol) was added to a solution of the methanesulfonate **3b** (4.59 g, 14.79 mmol) in dry dichloromethane (75 ml) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and 4 h at 20 °C before the mixture was worked up as in method B above. Distillation gave 1.73 g (55 %) of the product **4b**, b.p. 68 °C/ 1.1 mmHg.

2,2,2-Trifluoro-1,1-bis-(1,3-dithian-2-yl)ethanol (**5**). 1,3-Dithiane (3.00 g, 24.95 mmol) in dry THF (90 ml) was lithiated with butyllithium following the procedure given for **1** above. Trifluoroacetic acid anhydride (1.65 ml, 11.88 mmol) in dry THF (10 ml) was added slowly to the reaction mixture at −78 °C. After 15 h at −78 °C and 1 h at 0 °C, the reaction mixture was poured into ice–water (100 ml), neutralized with 3 M hydrochloric acid and extracted with dichloromethane (3 × 100 ml). The dried ($MgSO_4$) solution was concentrated and the crude product was purified by column chromatography (SiO_2; dichloromethane–hexane 3:2). Yield 1.28 g (32 %), m.p. 104 °C. ^{1}H NMR ($CDCl_3$): δ 1.8–2.2 (4 H, m), 2.7–3.1 (9 H, m), 4.66 (2 H, s). MS: 336 (1, *M*), 229 (22), 121 (8), 120 (5), 119 (100), 106 (1), 91 (3).

3,3,3-Trifluoropropanoic acid[2g,3b] (**6a**). Sulfuric acid (2 M, 10 ml) and mercury(II) oxide (4.54 g, 20.97 mmol) were added to a solution of 2-(2,2,2-trifluoroethylidene)-1,3-dithiane (2.00 g, 9.99 mmol) in THF (40 ml). The reaction mixture was refluxed for 26 h with good stirring, cooled, and filtered, and the precipitate washed with THF (10 ml) and diethyl ether (3 × 10 ml). The combined organic layers were washed with saturated aqueous sodium chloride (50 ml), the layers separated, and the aqueous layer extracted with diethyl ether (3 × 10 ml). After the combined ethereal extracts had been dried ($MgSO_4$) the solvent was removed by distillation (1 atm). The crude product was dissolved in sodium hydroxide (1 M, 10 ml) and the solution was washed with diethyl ether (3 × 5 ml), acidified with hydrochloric acid (1 M, 10 ml) and extracted with diethyl ether (4 × 10 ml). After the ethereal extracts had been dried ($MgSO_4$), the solvent was removed by distillation (1 atm) and the product distilled under reduced pressure to give 0.77 g (60 %) of **6a**, b.p. 80 °C/55 mmHg. Anal. $C_3H_3F_3O_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 3.25 (2 H, q, *J* 10 Hz), 9.25 (variable: 9.25–11.7, 1 H, s, br). MS: 128 (13, *M*), 111 (45), 91 (14), 89 (20), 83 (21), 69 (25), 64 (82), 45 (100).

3,3,3-Trifluoro-2-methylpropanoic acid[3g] (**6b**). Compound **6b** was obtained from 2-(2,2,2-trifluoro-1-methylethylidene)-1,3-dithiane using the procedure given above for **6a**. The crude product was purified by Kugelrohr distillation (80 °C/40 mmHg). Yield 40 %. Mol. wt., obs. 142.0237. Calc. for $C_4H_5F_3O_2$: 142.0242. ^{1}H NMR ($CDCl_3$): δ 1.45 (3 H, d *J* 7 Hz), 3.26 [1 H, septet (deg. qq), *J* 7 Hz], 11.42 (1 H, s). MS: 142 (4, *M*), 125 (24), 122 (21), 103 (10), 102 (51), 97 (15), 79 (2), 78 (65), 77 (100).

2-(2,2,2-Trifluoroethyl)-1,3-dithiane (**7a**): *Method A*. Sodium borohydride pellets (2.97 g, 78.61 mmol) were cautiously added to trifluoroacetic acid (60 ml) under nitrogen at 0 °C, before a solution of 2-(2,2,2-trifluoroethylidene)-1,3-dithiane (3.00 g, 14.98 mmol) in dry dichloromethane (40 ml) was added. After 15 min at 0 °C, and 1 h at ambient temperature all the sodium borohydride had dissolved and the solvent was removed under reduced pressure. The residue was poured into ice–water, and stirred for 1 h. The mixture was neutralized with aqueous sodium hydroxide (5 M) and extracted with hexane (6 × 50 ml). The combined extracts were dried ($MgSO_4$) and concentrated and the residue was distilled to give 1.97 g (65 %) of the product **7a**, b.p. 83 °C/8 mmHg. Anal. $C_6H_9F_3S_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.7–3.1 (8 H, m), 4.28 (1 H, t, *J* 7 Hz). MS: 202 (100, *M*), 169 (3), 160 (2), 155 (13), 128 (14), 127 (15), 119 (77), 74 (79).

Method B. Triethylsilane (2.56 g, 22.00 mmol) was added to 2-(2,2,2-trifluoroethylidene)-1,3-dithiane (4.00 g, 20.00 mmol) in dry dichloromethane (40 ml), before trifluoroacetic acid (11.40 g, 100.00 mmol) was added at 0 °C. After 15 min at 0 °C and 15 h at ambient temperature the reaction mixture was poured into saturated aqueous sodium hydrogen carbonate (100 ml) and extracted with dichloromethane (3 × 50 ml). The dichloromethane solution was washed with saturated aqueous sodium hydrogen carbonate (50 ml) and dried ($MgSO_4$). Concentration and distillation of the residue gave 1.45 g (35 %) of the product **7a**.

2-(2,2,2-Trifluoro-1-methylethyl)-1,3-dithiane (**7b**). Sodium borohydride pellets (1.59 g, 42.00 mmol) were cautiously added to trifluoroacetic acid (40 ml) under nitrogen at 0 °C, before 2-(2,2,2-trifluoro-1-methylethylidene)-1,3-dithiane (1.50 g, 7.00 mmol) in dry dichloromethane (20 ml) was added. After 15 min at 0 °C and 3 h at ambient temperature more sodium borohydride pellets (1.59 g, 42.00 mmol) were added. After a further 20 h at ambient temperature, the reaction mixture was worked up as in method A above. After the organic extracts had been dried ($MgSO_4$) and concentrated the crude product was purified by Kugelrohr distillation (100 °C/8 mmHg) to give 1.28 g (85 %) of the product **7b**. Mol. wt., obs. 216.0246. Calc. for $C_7H_{11}F_3S_2$: 216.0254. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (3 H, d, *J* 7.1 Hz), 1.8–1.9 (1 H, m), 2.1–2.15 (1 H, m) 2.5–2.7 (1 H, m), 2.8–3.1 (4 H, m), 4.48 (1 H, d, *J* 2.9 Hz). MS: 216 (37, *M*), 169 (2), 142 (3), 141 (5), 122 (3), 121 (11), 120 (6), 119 (100).

1,1-Diethoxy-3,3,3-trifluoropropane (**8a**). Mercury(II) chloride (4.03 g, 14.83 mmol) and red mercury(II) oxide (1.61 g, 7.42 mmol) were added, under nitrogen, to a solution of 2-(2,2,2-trifluoroethyl)-1,3-dithiane (1.00 g, 4.94 mmol) in absolute ethanol (50 ml). The reaction mixture was heated under reflux for 3 days with good stirring, cooled to 0 °C and filtered. The filtrate was poured into saturated aqueous sodium hydrogen carbonate (100 ml) and stirred for 15 min. The mixture was then filtered and extracted with hexane (8 × 50 ml). After the combined organic extracts had been dried (K_2CO_3), the solvent was removed by distillation (1 atm). The crude product was purified by Kugelrohr distillation (130 °C/1 atm) with solid CO_2 cooling to give 0.25 g (27 %) of the product **8a**. Mol. wt., obs. 185.0796. Calc. for $C_7H_{12}F_3O_2$ (*M*−H): 185.0789. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (6 H, t, *J* 7.0 Hz), 2.46 (2 H, qd, *J* 10.7, 5.5 Hz), 3.5–3.7 (4 H, m), 4.82 (1 H, t, *J* 5.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.0 (CH_3), 38.6

(CH_2, q, J 27 Hz), 61.8 (CH_2O), 97.2 (CH, q, J 4 Hz), 125.2 (CF_3, q, J 276 Hz). MS: 185 (0.1, $M-1$), 157 (0.3), 143 (0.2), 142 (3), 141 (51), 129 (2), 114 (3), 113 (100), 103 (29), 93 (39). MS (CI-NH_3): 204 (18, $M + NH_4^+$), 158 (17), 141 (12), 129 (17), 121 (14), 112 (6), 109 (25), 103 (100).

1,1-Diethoxy-3,3,3-trifluoro-2-methylpropane[11] (**8b**). Compound **8b** was prepared from 2-(2,2,2-trifluoro-1-methylethyl)-1,3-dithiane **7b** using the procedure given above for **8a**, except that the heating was limited to 2 days. The crude product was purified by Kugelrohr distillation (85 °C/70 mmHg) to give 0.31 g (33 %). Mol. wt., obs. 199.0931. Calc. for $C_8H_{14}F_3O_2$ ($M-H$): 199.0946. ^1H NMR (300 MHz, $CDCl_3$): δ 1.17 (3 H, d, J 7.1 Hz), 1.21 (3 H, t, J 7.0 Hz), 1.22 (3 H, t, J 7.0 Hz), 2.4–2.6 (1 H, m), 3.5–3.6 (2 H, m), 3.65–3.8 (2 H, m), 4.58 (1 H, d, J 5.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.8 (CH_3), 15.0 (CH_3), 42.3 (CF_3CH, q, J 25 Hz), 63.0 (CH_2), 63.5 (CH_2), 100.9 (CF_3CHCH, q, J 3 Hz), 126.8 (CF_3, q, J 280 Hz). MS: 199 (0.2, $M-1$), 171 (0.6), 156 (4), 155 (59), 128 (4), 127 (98), 107 (69), 103 (54), 79 (43), 75 (46), 47 (100), MS (CI–NH_3): 218 (22, $M+NH_4^+$), 173 (3), 172 (34), 155 (24), 143 (69), 135 (43), 132 (14), 126 (44), 123 (34), 106 (10), 104 (8), 103 (100).

2-(2-Oxo-1-trifluoromethylpropylidene)-1,3-dithiane (**9**). Zinc chloride (136 mg, 1.0 mmol) was added to a solution of 2-(2,2,2-trifluoroethylidene)-1,3-dithiane **4a** (200 mg, 1.0 mmol) in acetyl chloride (3 ml). The mixture was heated at 65 °C for 18 h before the acetyl chloride was evaporated off. The residue was dissolved in acetone, poured into saturated aqueous sodium hydrogen carbonate and extracted with diethyl ether. The ether solution was washed consecutively with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, then dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography (SiO_2; hexane–EtOAc 5:1). Yield 172 mg (71 %), m.p. 37 °C. Anal. $C_8H_9F_3OS_2$: C, H. ^1H NMR (300 MHz, $CDCl_3$): δ 2.24 (2 H, tt, J 7.0, 7.0 Hz), 2.34 (3 H, q, J 2.0 Hz), 2.91 (2 H, t, J 7.0 Hz), 3.03 (2 H, t, J 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.6, 29.2 and 29.5 ($SCH_2CH_2CH_2S$), 29.7 (CH_3, q, J 4 Hz), 123.2 (CF_3, q, J 274 Hz), 124.3 ($CF_3C=$, q, J 31 Hz), 168.1 ($CF_3C=C$), 192.4 (C=O). MS: 242 (49, M), 229 (7), 228 (7), 227 (76), 209 (8), 200 (6), 181 (4), 157 (4), 153 (34), 43 (100). IR (cm^{-1}, KBr): 1645, 1652 and 1690.

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