Synthesis of 3-(Alkylthio and Phenylthio)-1,1,1-trifluoroalkan-2-ones via Ring Opening of Epoxy Ethers

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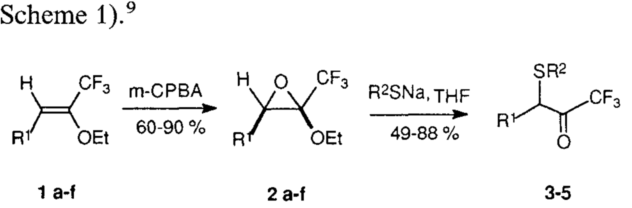
Regioselective ring opening of 1-trifluoromethyl epoxy ethers **2** was achieved with alkyl and phenyl sodium thiolates to afford new 3-(alkylthio and phenylthio)-1,1,1-trifluoroalkan-2-ones **3–5** in good yields.

Polarized ketones, such as trifluoromethyl ketones, tend to undergo hydration, and are putative isosteric analogues of tetrahedral intermediates formed during the hydrolysis of esters and amides.[1,2] Trifluoromethyl ketones are inhibitors of a variety of serine esterases, such as juvenile hormone esterase[3] and mammalian carboxyl esterases.[4] Hammock et al. demonstrated that the introduction of a sulfur atom in the α-position of these ketones increases the potency of juvenile hormone esterase inhibitors in comparison with simple aliphatic trifluoromethyl ketones.[3] The inhibition activity of 3-(alkylthio)-1,1,1-trifluoromethylalkan-2-ones and corresponding alcohols has been confirmed several times.[5–8]

All α-thiosubstituted trifluoromethyl ketones have previously been prepared by the reaction of a thiol with an α-bromo trifluoromethyl ketone. Despite a recent improvement in the preparation of these α-bromo ketones,[9] their availability is still problematic because of their instability.

Herein we report on a new and convenient method for the synthesis of α-thiosubstituted trifluoromethyl ketones, based on the nucleophilic ring opening of 1-CF_3-epoxy ethers **2**, which have already been shown to be suitable synthetic intermediates for the preparation of CF_3-containing organic compounds.[9–11] These epoxy ethers **2** are readily available by a Wittig olefination of alkyl trifluoroacetates, leading to enol ethers **1**,[12] followed by *m*-chloroperbenzoic acid (*m*-CPBA) epoxidation (Scheme 1).[9]



1,2	R¹	R² 3	4	5
a	Ph	Ph	n-Hexyl	n-Octyl
b	-CH_2-CH_2-C_6H_5	Ph	n-Hexyl	n-Octyl
c	CH_2-C_6H_5	Ph		
d	CH_2-CH_2-C_6H_4-OMe	Ph		
e	n-Hexyl	Ph		
f	CH_2-Cyclohexyl	Ph		

Scheme 1

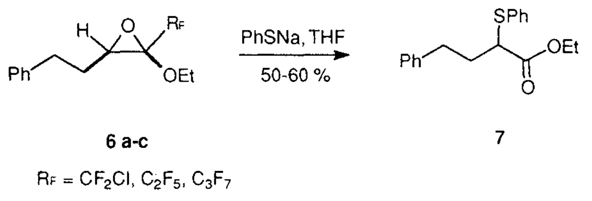
Table 1. Reaction of Sodium Thiolate (R^2SNa) with Epoxy Ethers **2**

Starting Material	Product[a] 3–5	Time (min)	Yield[b] (%)
2a	**3a**	5	88
2a	**4a**	10	81
2a	**5a**	10	82
2b	**3b**	10	85
2b	**4b**	30	58
2b	**5b**	30	49
2c	**3c**	30	75
2d	**3d**	30	86
2e	**3e**	30	82
2f	**3f**	30	81

[a] Satisfactory microanalyses obtained: C ± 0.33, H ± 0.16.
[b] Yield of isolated product.

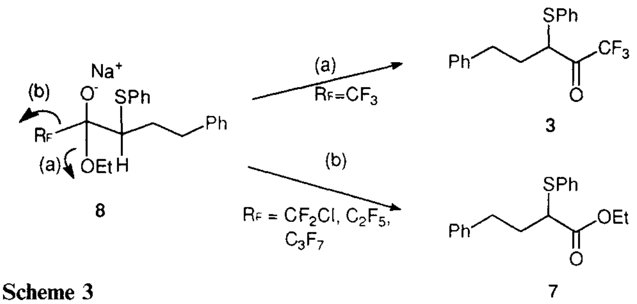
We have investigated the reaction of epoxides **2a–e** with thiols under different conditions. We found that they were unreactive towards thiols even when catalysed by metal salts, such as lithium perchlorate.[13] However, treatment of epoxy ethers **2a–f** with sodium thiolates led to the new alkylthio and arylthio ketones **3–5**. This reaction proceeded at room temperature during 5–30 minutes in moderate to good yields depending on the substituent pattern (Scheme 1, Table 1). The most reactive thiolate is the sodium thiophenolate (R^2 = Ph), which provides high yields from all epoxy ethers **2**. The reactivity of sodium alkyl thiolates depends on the substitutent R^1 of epoxy ethers **2**; yields are higher when R^1 is a phenyl group.

We have also investigated under similar conditions the reaction of sodium thiophenolate with 1-perfluoroalkyl epoxy ethers **6a–c** (Scheme 2). The reaction was slower than in the case of 1-CF_3-epoxy ethers. At room temperature and with one or several equivalents of base, starting materials were recovered. At 45–50 °C, with one equivalent of base, epoxy ethers **6a–c** reacted partially, with 2 equivalents of sodium thiophenolate the starting epoxy ethers **6a–c** completely disappeared. Surprisingly the expected (α-phenylthio)ketones were not detected, the only isolated product was the ethyl (2-phenylthio)carboxylate **7**.



Scheme 2

The formation of this product indicates that the elimination of the perfluoroalkyl group is faster than that of the ethoxide anion from the tetrahedral intermediate **8** (Scheme 3). This haloform-type reaction is well-known with trihalogenoalkyl ketones in the presence of base.[14] These results give additional evidence of the different reaction behaviour of CF_3- and other perfluoroalkyl-containing compounds.[11,15]



Scheme 3

^{19}F NMR, ^{31}P NMR, ^{1}H NMR and ^{13}C NMR spectra were recorded on a 200 MHz multinuclear sprectrometer. ^{19}F NMR spectra are referenced to external $CFCl_3$, ^{1}H NMR and ^{13}C NMR spectra to TMS, and ^{31}P NMR spectra to H_3PO_4. In all NMR measurements $CDCl_3$ was used as a solvent. GC analyses were performed using a SE 30 capillary column (25 m).

THF was purified by distillation from sodium benzophenone ketyl. All the reactions with NaH were performed in an oven-dried apparatus. NaH was washed with pentane from a suspension in mineral oil obtained from Fluka. Fluorinated esters are available from Aldrich or prepared by classical procedures[16] and used after treatment with anhyd K_2CO_3.

2-Phenylethyltriphenylphosphonium Bromide:

A solution of (2-bromoethyl)benzene (100 mmol, 18.5 g) and Ph_3P (105 mmol, 27.5 g) in anhyd toluene (100 mL) was refluxed for 48 h. After cooling, the upper layer was removed, toluene (50 mL) was added and the mixture obtained was refluxed for 10 min. After decantation and separation, the residue obtained was washed again with toluene and then with anhyd pentane (3 x 50 mL). The remaining solvent of the residue thus obtained was evaporated. The resulting phosphonium salt was obtained as a very hygroscopic "glassy" compound; yield: 35.8 g (80 %).

^{1}H NMR: $\delta = 3.05$ (m, 2 H), 4.15 (m, 2 H), 7.15 (m, 5 H), 7.73 (m, 15 H).

^{31}P NMR: $\delta = 22.1$.

(*Z*)-2-Ethoxy-1,1,1-trifluoronon-2-ene (1 e); Typical Procedure:

A dry 250 mL, three-necked, round-bottomed flask containing a Teflon-covered magnetic stirring bar and equipped with a rubber septum inlet and $CaCl_2$ drying tube was flushed with dry Ar and charged with NaH (2.31 g, 80 % dispersion in mineral oil, 77 mmol). The content of the flask was washed twice with anhyd pentane. The flask was then charged with THF (100 mL), heptyltriphenylphosphonium bromide (31.57 g, 70 mmol) and equipped with a condenser. The mixture was stirred under reflux for 5 h and cooled with an ice bath. Ethyl trifluoroacetate (10.0 g, 70 mmol) was slowly added through the septum inlet. The ice bath was removed, and the mixture was refluxed for 1 h, cooled and diluted with pentane (300 mL). The solution was filtered through a short silica gel column. Then the column was washed with a mixture of pentane/Et_2O (5 : 1, 200 mL). Evaporation of the solvent under reduced pressure and then bulb-to-bulb distillation at 10 Torr (bath temperature 110–130 °C) provided **1e** as a colorless liquid; bp 90 °C/(10 Torr); yield: 8.54 g (54 %) (Table 2).

(Z)-1,1,1-Trifluoro-2-ethoxy-4-phenylbut-2-ene (**1c**); purified by flash chromatography on silica gel (eluent: pentane/Et_2O, 20 : 1); yield: 47 %.

(Z)-1,1,1-Trifluoro-2-ethoxy-5-(4-methoxyphenyl)pent-2-ene (**1d**); yield: 55 %; b 90 °C/1 Torr.

Enol ethers **1a, b, e, f** have been described.[12]

2,3-Epoxy-2-ethoxy-1,1,1-trifluorononane (2e); Typical Procedure:

A 250 mL round-bottomed flask was equipped with magnetic stirring bar and condenser with $CaCl_2$ drying tube. The flask was charged with **1e** (9.2 g, 40 mmol), *m*-CPBA (14.79 g, 60 mmol), and CH_2Cl_2 (170 mL). The reaction mixture was refluxed with stirring for 20 h, cooled, concentrated under reduced pressure to a volume of 50–60 mL, diluted with pentane (200 mL) and passed through a short silica gel column. Then the column was washed with a mixture of pentane/Et_2O (5 : 1, 100 mL). Evaporation of solvents under reduced pressure and bulb-to-bulb distillation at 10 Torr (bath temperature 110–130 °C) provided **2e** as a clear colorless liquid; bp 95 °C/10 Torr; yield: 9.15 g (90 %) (Table 2).

2,3-Epoxy-1,1,1-trifluoro-2-ethoxy-4-phenylbutane (**2c**); yield: 92 %.

Table 2. NMR Data of Enol Ethers 1 and Epoxy Ethers 2.

Product	^{19}F NMR ($CDCl_3/CFCl_3$) (186 MHz), δ	^{1}H NMR ($CDCl_3$/TMS) (200 MHz) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) (100 MHz) δ, $J_{C,F}$ (Hz)
1c	– 68.5	1.30 (t, $J = 7$, 3 H), 3.54 (d, $J = 7.5$, 1 H), 3.55 (d, $J = 7.5$, 1 H), 3.97 (q, $J = 7$, 2 H), 5.86 (t, $J = 7.5$, 1 H), 7.23 (m, 5 H)	15.3, 35.5, 69.5, 121.2 (q, $^{1}J = 275$, CF_3), 126.5, 128.5, 128.7, 141.2, 143.6 (q, $^{2}J = 32$, $\underline{C}-CF_3$)
1d	– 69.7	1.28 (t, $J = 7$, 3 H), 2.41 (m, 2 H), 2.68 (m, 2 H), 3.74 (s, 3 H), 3.77 (q, $J = 7$, 2 H), 5.66 (t, $J = 7$, 1 H), 6.78 (m, 2 H), 7.16 (m, 2 H)	15.5, 27.0, 34.0, 55.4, 69.8, 114.0, 121.9 (q, $^{1}J = 275$, Hz, CF_3), 129.3, 129.33, 133.0, 142.4 (q, $^{2}J = 32$, $\underline{C}-CF_3$), 158.1
1e	– 69.8	0.83 (t, $J = 7.5$, 3 H), 1.28 (t, $J = 7$, 3 H), 1.35 (m, 8 H), 2.11 (m, 2 H), 3.81 (q, $J = 7$, 2 H), 5.59 (t, $J = 7$, 1 H)	13.9, 15.5, 22.4, 24.6, 28.6, 28.8, 31.4, 69.6, 121.0, 121.1 (q, $^{1}J = 277$, CF_3), 149.4 (q, $^{2}J = 32$, $\underline{C}-CF_3$)
2c	– 77.9	1.25 (t, $J = 7$, 3 H), 2.93 (d, $J = 6.2$, 2 H), 3.38 (t, $J = 6.2$, 1 H), 3.80 (q, $J = 7$, 2 H), 7.25 (m, 5 H)	15.5, 33.4, 62.0, 64.2, 81.8 (q, $^{2}J = 40$, C-CF_3), 122.1 (q, $^{1}J = 282$, CF_3), 127.2, 129.0, 129.1, 136.1
2d	– 76.8	1.21 (t, $J = 7$), 1.88 (m, 2 H), 2.65 (m, 2 H), 3.2 (t, $J = 6.1$, 1 H), 3.77 (s, 3 H), 3.80 (q, $J = 7$, 2 H), 6.79 (m, 2 H), 7.11 (m, 2 H)	15.2, 28.5, 30.8, 55.1, 61.1, 63.7, 81.1, (q, $^{2}J = 40$, $\underline{C}-CF_3$), 113.9, 121 (q, $^{1}J = 280$, CF_3), 129.2, 132.4, 159.5
2e	– 77.1	0.85 (t, $J = 7.5$, 3 H), 1.25 (t, $J = 7$, 3 H), 1.32 (m, 8 H), 1.61 (m, 2 H), 3.12 (t, $J = 6.2$, 1 H), 3.82 (q, $J = 7$, 2 H)	14.1, 15.4, 22.6, 25.7, 26.5, 26.6, 29.0, 31.7, 62.2, 63.8, 81.7 (q, $^{2}J = 40$, $\underline{C}-CF_3$), 122.0 (q, $^{1}J = 282$, CF_3)

[a] Satisfactory microanalyses obtained: C ± 0.29, H ± 0.14.

2,3-Epoxy-1,1,1-trifluoro-2-ethoxy-5-(4-methoxyphenyl)pentane (**2d**); yield: 60%; bp 90°C/1 Torr.

Epoxy ethers **2a, b, e, f** and **6a–c** have been described.[9,17]

6-Phenyl-3-(phenylthio)-1,1,1-trifluorohexan-2-one (3b); Typical Procedure:

NaH (300 mg, 80% dispersion in mineral oil, 10 mmol) was placed in an Ar-flushed three-necked flask and washed twice with anhyd pentane. THF (50 mL) was added via syringe through a septum cap. The suspension was cooled to 0°C and thiophenol (1.03 mL, 10 mmol) was added dropwise. The mixture was stirred for about 0.5 h at r.t. and the epoxy ether **2b** (2.34 g, 9.0 mmol) was added in one portion to the suspension of sodium thiophenolate. After 10 min the precipitate disappeared and the reaction mixture was quenched with aq NH_4Cl. The organic phase was washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography on silica gel (pentane/Et_2O, 50:1, 20:1) to afford **3b** after evaporation of solvents; yield: 2.48 g (85%) (Table 3).

Reaction of Epoxy Ethers 6a–c with Sodium Thiophenolate; Ethyl 4-phenyl-2(phenylthio)butyrate (7):

NaSPh (2 equiv) prepared from NaH and thiophenol as described above was heated with epoxy ethers **6a–c** at 45–50°C for 30 min and quenched with aq NH_4Cl. The organic phase was washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography on silica gel (pentane/Et_2O, 20:1, 10:1) to afford **7** after evaporation of the solvent; yield: 50–60%.

IR (neat): $\nu = 1735\ cm^{-1}$ (C=O).

^1H NMR: $\delta = 1.21$ (t, $J = 7$ Hz, 3H), 2.02–2.35 (m, 2H), 2.77 (t, $J = 7.3$ Hz, 2H), 3.75 (t, $J = 7$ Hz, 1H), 4.15 (q, $J = 7$ Hz, 2H), 7.15–7.35 (m, 8H), 7.37–7.50 (m, 2H).

^{13}C NMR: $\delta = 15.1, 25.5, 33.0, 49.8, 61.0, 126.0, 127.8, 128.3, 128.4, 128.5, 128.8, 128.9, 132.8, 133.1, 140.5, 171.9$ (C=O).

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Table 3. IR and NMR Data of Compounds **3–5**

Product	IR (neat) $\nu_{C=O}$ (cm^{-1})	^{19}F NMR $CDCl_3/CFCl_3$ (186 MHz) δ	^1H NMR ($CDCl_3$/TMS) (200 MHz) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) (50 MHz) δ, $J_{C,F}$ (Hz)
3a	1745	– 75.8	5.19 (s, 1H), 7.22–7.45 (m, 10H)	57.0, 115.6 (q, $^1J = 293$, CF_3), 129.0, 129.2, 131.5, 132.6, 134.3, 185.2 (q, $^2J = 33$, $\underline{C}-CF_3$)
4a	1745	– 75.4	0.88 (t, $J = 7.5$, 3H), 1.05–1.32 (m, 6H), 1.41 (m, 2H), 2.46 (t, $J = 7.2$, 2H), 4.96 (s, 1H), 7.15–7.51 (m, 5H)	13.9, 22.4, 28.3, 28.6, 31.2, 31.5, 52.2, 115.6 (q, $^1J = 292$, CF_3), 128.7, 128.8, 129.0, 133.0, 185.1 (q, $^2J = 33$, $\underline{C}-CF_3$)
5a	1745	– 75.4	0.89 (t, $J = 7.5$, 3H), 1.05–1.37 (m, 10H), 1.48 (m, 2H), 2.45, (t, $J = 7.2$, 2H), 4.93 (s, 1H), 7.15–7.35 (m, 5H)	14.0, 22.6, 28.5, 28.6, 28.8, 29.0, 31.4, 31.7, 52.1, 115.8 (q, $^1J = 293$, CF_3), 126.8, 128.4, 128.7, 128.74, 128.9, 132.9, 185.5 (q, $^2J = 34$, $\underline{C}-CF_3$)
3b	1745	– 74.8	2.08 (tt, $J = 7.0$, 7.3, 2H), 2.75 (t, $J = 7.3$, 2H), 3.82 (t, $J = 7.0$, 1H), 7.11–7.48 (m, 10H)	30.4, 32.5, 49.0, 115.6 (q, $^1J = 293$, CF_3), 126.4, 128.2, 128.3, 128.6, 129.2, 129.8, 135.9, 139.8, 185.4 (q, $^2J = 34$, $C-CF_3$)
4b	1745	– 74.8	0.89 (t, $J = 7.5$, 3H), 1.04–1.32 (m, 6H), 1.42 (m, 2H), 2.02 (tt, $J = 7.0$, 7.3, 2H), 2.22 (m, 1H), 2.35 (m, 1H), 2.67 (t, $J = 7.3$, 2H), 3.47 (t, $J = 7.0$, 1H), 7.05–7.31 (m, 5H)	13.9, 22.4, 28.4, 28.7, 30.0, 31.2, 32.7, 45.3, 115.4 (q, $^1J = 292$, CF_3), 126.5, 128.4, 128.4, 128.6, 140.1, 185.2 (q, $^2J = 34$, $\underline{C}-CF_3$)
5b	1745	– 74.7	0.89 (t, $J = 7.5$, 3H), 1.08–1.38 (m, 10H), 1.44 (m, 2H), 2.02 (tt, $J = 7.0$, 7.3, 2H), 2.21 (m, 1H), 2.33 (m, 1H), 2.65 (t, $J = 7.3$, 2H), 3.45 (t, $J = 7.0$, 1H), 7.11–7.32 (m, 5H)	14.2, 22.7, 28.5, 28.7, 28.9, 29.4, 30.2, 31.5, 32.2, 33.0, 45.3, 116.0 (q, $^1J = 292$, CF_3), 126.7, 128.6, 128.9, 140.3, 185.1 (q, $^2J = 33$, $\underline{C}-CF_3$)
3c	1745	– 75.5	3.12 (ddd, $J = 12.0$, 7.1, 7.3, 2H), 4.15 (dd, $J = 7.1$, 7.3, 1H), 7.15–7.51 (m, 10H)	35.7, 51.4, 115.4 (q, $^1J = 293$, CF_3), 127.0, 127.1, 127.4, 128.6, 128.9, 129.0, 129.1, 129.2, 129.8, 129.82, 135.8, 136.7, 185.2 (q, $^2J = 33$, $\underline{C}-CF_3$)
3d	1745	– 74.8	2.11 (td, $J = 7.0$, 7.3, 2H), 2.75 (t, $J = 7.3$, 2H), 3.82 (s, 3H), 3.84 (t, $J = 7.0$, 1H), 6.9 (m, 2H), 7.11 (m, 2H), 7.35–7.51 (m, 5H)	30.8, 31.8, 49.1, 55.5, 115.4 (q, $^1J = 293$, CF_3), 114.3, 128.4, 129.5, 129.6, 130.1, 132.1, 136.3, 158.4, 185.4 (q, $^2J = 34$, $\underline{C}-CF_3$)
3e	1745	– 75.3	0.89 (t, $J = 7.5$, 3H), 1.15–1.52 (m, 8H), 1.68 (m, 2H), 3.75 (t, $J = 7.0$, 1H), 7.21–7.42 (m, 5H)	13.9, 22.4, 26.6, 28.7, 29.0, 31.4, 50.1, 115.7 (q, $^1J = 292$, CF_3), 128.7, 129.1, 129.7, 132.8, 135.8, 185.7 (q, $^2J = 33$, $C-CF_3$)
3f	1745	– 74.9	0.71–1.75 (m, 13H), 3.98 (t, $J = 7.0$, 1H), 7.27–7.47 (m, 5H)	26.1, 26.3, 26.6, 33.1, 33.2, 35.1, 36.7, 48.0, 115.9 (q, $^1J = 292$, CF_3), 129.0, 129.4, 130.0, 136.1, 185.9 (q, $^2J = 33$, $\underline{C}-CF_3$)

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