Supporting Information

Alkoxide and Hydroxide Induced Nucleophilic Trifluoromethylation Using Trifluoromethyl Sulfone or Sulfoxide

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General:

Unless otherwise mentioned, all other chemicals were purchased from commercial sources. Potassium *tert*-butoxide (95 %) was used as received. DMF was distilled over calcium hydride, and stored over activated molecular sieve. Phenyl trifluoromethyl sulfone (**1a**) or sulfoxide (**1b**) was prepared by the oxidation of phenyl trifluoromethyl sulfide with hydrogen peroxide or *m*CPBA.^{1,2} Methyl trifluoromethyl sulfone (**1c**) was prepared using known procedures.³ Most of the trifluorinated products are known, and their characterization results are consistent with the reported data.⁴⁻⁸

¹H, ¹³C and ¹⁹F NMR spectra were recorded on superconducting NMR spectrometers at either 500 or 360 MHz. ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0 or to the signal of a residual protonated solvent: CDCl₃ δ 7.26. ¹³C NMR chemical shifts were determined relative to internal

TMS at δ 0.0 or to the ^{13}C signal of solvent: CDCl_3 δ 77.0. ^{19}F NMR chemical shifts were determined relative to internal CFCl_3 at δ 0.0. The ^{19}F NMR yields were determined by the integration of the corresponding product peaks with respect to PhOCF_3 internal standard. Mass spectra were recorded on GC-MS spectrometer with a mass selective detector at 70 eV.

Typical procedures for $t\text{BuOK}$ induced trifluoromethylation:

The reaction was commonly carried out in a Schlenk flask under an argon atmosphere. Into 7 ml DMF solution of phenyl trifluoromethyl sulfone (**1a**, 420 mg, 2 mmol) and 4-methylbenzophenone (196 mg, 1 mmol) at $-50\text{ }^\circ\text{C}$, was added 3 ml DMF solution of $t\text{BuOK}$ (280 mg, 2.5 mmol). The reaction flask was then sealed and the reaction mixture was then stirred from $-50\text{ }^\circ\text{C}$ for 1h, followed by stirring at $-50\text{ }^\circ\text{C}$ to room temperature overnight. The reaction mixture was quenched with 10 ml of ice water, and extracted with ether (20 ml x 3). The combined ether phase was washed with saturated NH_4Cl aqueous solution, followed by washing with water. After drying over MgSO_4 , the ether solvent was removed under vacuum. The crude product was further purified by column chromatography (hexanes/ether = 9/1) to give 225 mg of product, 4-methyl- α -phenyl- α -(trifluoromethyl)benzenemethanol as a colorless oily liquid, yield 85 %. ^1H NMR (CDCl_3): δ 3.01 (b, 1H); 7.35-7.38 (m, 6H); 7.49-7.52 (m, 4H). ^{19}F NMR (CDCl_3): δ - 74.5. MS: 252 (M^+).

Other products:

1-Phenyl-2,2,2-trifluoroethanol:⁴ yellow oily liquid, 77 % yield. ¹H NMR (CDCl₃): δ 2.86 (s, 1H); 5.01 (q, ³J_{H-F} = 6.3 Hz, 1H); 7.43 (m, 2H); 7.48 (m, 3H). ¹⁹F (CDCl₃): δ -78.5 (d, ³J_{H-F} = 6.2 Hz). MS: 176 (M⁺).

1-(2'-Naphthyl)-2,2,2-trifluoroethanol:⁴ yellow solid, 62 % yield. ¹H NMR (CDCl₃): δ 2.76 (b, 1H); 5.19 (q, ³J_{H-F} = 6.7 Hz, 1H); 7.51-7.96 (m, 7H). ¹⁹F (CDCl₃): δ -78.4 (d, ³J_{H-F} = 6.7 Hz). MS: 226 (M⁺).

4'-Ethyl-phenyl-2,2,2-trifluoroethanol:⁵ oily liquid, 83 % yield. ¹H NMR (CDCl₃): δ 1.25 (t, 3H); 2.60 (b, 1H); 2.67 (q, 2H); 4.99 (m, 1H); 7.25 (d, 2H); 7.38 (d, 2H). ¹⁹F NMR (CDCl₃): δ -78.9 (d, ³J_{H-F} = 7.7 Hz). ¹³C NMR (CDCl₃): δ 15.4; 28.6; 72.6 (q, J = 31.9 Hz); 124.3 (q, J = 282.5 Hz); 127.4; 128.1; 131.2; 145.8. MS: 204 (M⁺).

4'-Biphenyl-2,2,2-trifluoroethanol:⁶ white solid, 76 % yield. ¹H NMR (CDCl₃): δ 2.87 (b, 1H); 5.07 (m, 1H); 7.40-7.65 (m, 9 H). ¹⁹F NMR (CDCl₃): δ -78.7 (d, J = 7.6 Hz). ¹³C NMR (CDCl₃): δ 72.6 (q, J = 31.6 Hz); 124.3 (q, J = 281.8 Hz); 127.1; 127.3; 127.7; 127.8; 128.8; 132.8; 140.3; 142.5. MS: 252 (M⁺).

α-Phenyl-α-(trifluoromethyl)benzenemethanol:⁴ oily liquid, 86 % yield. ¹H NMR (CDCl₃): δ 2.36 (s, 3H); 2.89 (s, 1H); 7.17-7.51 (m, 9H). ¹⁹F NMR (CDCl₃): δ -74.4. MS: 266 (M⁺).

4,4'-Dichloro-α-phenyl-α-(trifluoromethyl)benzenemethanol:⁷ pale yellow oily liquid, 74 % yield. ¹H NMR (CDCl₃): δ 2.95 (s, 1H); 7.34 (d, 4H); 7.40 (d, 4H). ¹⁹F NMR (CDCl₃): δ -75.1. MS: 320 (M⁺).

4-Nitro- α -phenyl- α -(trifluoromethyl)benzenemethanol: pale yellow oily liquid, 83 % yield. ^1H NMR (CDCl_3): δ 3.15 (s, 1H); 7.37-8.23 (m, 9 H). ^{19}F NMR (CDCl_3): δ - 74.7. MS: 297 (M^+).

4-Methoxy- α -phenyl- α -(trifluoromethyl)benzenemethanol:⁴ oily liquid, 73% yield. ^1H NMR (CDCl_3): δ 2.80 (s, 1H); 3.81 (s, 3H); 6.87-7.49 (m, 9 H). ^{19}F NMR (CDCl_3): δ - 75.0. MS: 281 ($\text{M}^+ - 1$).

2-(Trifluoromethyl)-2-adamantanol:⁴ 82 % yield, white solid (sublimed). ^1H NMR (CDCl_3): δ 1.56-2.27 (m, 15H). ^{19}F (CDCl_3): δ - 76.1. MS: 220 (M^+).

2,2,2-Trifluoroacetophenone:⁸ 82 % yield, colorless liquid. ^1H NMR (CDCl_3): δ 7.53 (t, J = 8.0 Hz, 2H); 7.70 (t, J = 7.5 Hz, 1H); 8.06 (d, J = 8.0 Hz, 2 H). ^{19}F (CDCl_3): δ - 71.8. MS: 174 (M^+).

Phenyl trifluoromethyl sulfide:² 87 % yield, colorless liquid. ^1H NMR (CDCl_3): δ 7.43 (t, J = 7.5 Hz, 2H); 7.50 (t, J = 7.5 Hz, 1H); 8.67 (d, J = 7.5 Hz, 2 H). ^{19}F (CDCl_3): δ - 43.2.

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