Supporting Information

for

Fluorous Dimethyl Sulfide: A Convenient, Odorless, Recyclable Borane Carrier

David Crich and Santhosh Neelamkavil*

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, ILL 60607-7061.

General Experimental
All reagents were purchased from commercial sources and used as received, unless otherwise indicated. Tetrahydrofuran was distilled from sodium/benzophenone ketyl, and methylene chloride was distilled from calcium hydride prior to use. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in deuteriochloroform solutions at 500 or 300, 125 or 75, and 282 MHz, respectively. All reactions were performed under a dry argon atmosphere unless otherwise indicated. All hydroboration substrates were either commercially available or prepared as described in the literature. With the exception of **11**, **13** and **14**, all products were identical to either commercial or literature samples.

***S*-[2-(Perfluorooctyl)ethyl] Thioacetate:** To a stirred solution of potassium thioacetate (1.0 g, 8.75 mmol) in DMF (100 mL) under Ar was added pefluorooctylethyl iodide (5.0 g, 8.70 mmol) at room temperature. After completion (2 h), the reaction mixture was taken up in ether (100 mL) and washed with sat. NH_4Cl (30 mL), brine (30 mL) and water (50 mL). Concentration of the organic layer followed by silica gel chromatography (hexanes: EtOAc 10:1) gave the known thioacetate[1] (3.7g, 81%) as a very pale yellow oil. ^{1}H NMR: δ 3.11-3.06 (m, 2H), 2.47-2.29 (m, 2H), 2.36 (s, 3H).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl Methyl Sulfide (1): To the above fluorous thioacetate (3.25 g, 6.20 mmol) dissolved in methanol (40 mL) and cooled to 0 ^{0}C Ar was added dropwise a freshly prepared solution of NaOMe (0.33g, 14.95 mmol) in methanol (6.3 mL). The reaction mixture was then stirred for 0.5 h before methyl iodide (2.1 g, 14.8 mmol) dissolved in methanol (5 mL) was added dropwise over a period of 10 min at 0 ^{0}C. After stirring at room temperature for 1 h the reaction mixture was poured into cold water and extracted with ether. Concentration of the ether layer followed by silica gel chromatography (hexanes : EtOAc 40 : 1) yielded the fluorous sulfide **1** (2.9 g, 94%) as a colorless oil. ^{1}H NMR: δ 2.74-2.69 (m, 2H), 2.47-2.33 (m, 2H), 2.16 (s, 3H); ^{13}C NMR: δ 120.2-104.6 (m), 31.8 (t), 24.8 (t), 15.5 (s); ^{19}F NMR: -8.3 (t), -41.9 (t), -49.3, -49.4, -49.5, -50.3, -51.0, -53.7. ESIMS Calcd. for $C_{11}H_7F_{17}S$ $[M-H]^+$: 493.1. Found 493.1.

Solid Mixture of Sulfide (1) and Borane-Sulfide (2): Diborane gas, generated by reaction of $NaBH_4$ (1.5 g, 39.0 mmol) in diglyme (12 mL) with BF_3:Et_2O (6 mL) was passed through the neat fluorous sulfide (**1**) (2.9 g, 5.88 mmol) at 25 ^{0}C for a period of 10 min after which the oily fluorous sulfide was converted into a white solid. ^{1}H NMR spectroscopy showed a 1:1 relation of **2**:**1** (coordinated:non-coordinated) and ^{11}B NMR showed a single resonance at δ –22.0 ppm corresponding to **2**. ESIHRMS Calcd. for $C_{11}H_{10}BF_{17}S$ $[M+H]^+$: 509.0403. Found 509.0295. The ^{1}H NMR spectrum of the mixture showed the above resonances for **1** and the following resonances for **2**: δ 2.89-2.83 (m, 1H), 2.77-2.71 (m, 1H), 2.62 (m, 2H), 2.35 (s, 3H).

Typical Procedure for the Hydroboration of Alkenes with the Mixture of 1 and 2; *S*-Ethyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(3-hydroxypropyl)-α-D-thiomannopyranoside *S*-Oxide (13) and *S*-Ethyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(2-hydroxypropyl)-α-D-thiomannopyranoside *S*-Oxide (14). To *S*-ethyl 2-*O*-allyl-3-

O-benzyl-4,6-*O*-benzylidene-α-D-thiomannopyranoside *S*-oxide[2] (0.15 g, 0.32 mmol) dissolved in a biphasic solvent system of CH_2Cl_2 (2 mL) and FC-72 (2 mL) under Ar was added the 1/1 mixture of **1** and **2** (0.1 g, 0.1 mmol of **2**) at 0 ^{0}C followed by stirring for 1 h. The FC-72 layer was then removed and the organic layer oxidized by adding 3 M NaOH (0.035 mL, 0.105 mmol) and 30% H_2O_2 (0.019 mL, 0.165 mmol) followed by stirring overnight. Evaporation of the FC-72 phase returned **1** (0.08 g, 80%). The CH_2Cl_2 layer was diluted with water (2 mL) and stirred for 0.5 h. Evaporation of the solvent followed by column chromatography (hexanes:EtOAc 40:1→3:1) gave the fluorous sulfide **1** (0.01 g, 10%) followed by the alcohols **13** (0.087g, 59%) and **14** (0.029g, 19%) in a 3:1 ratio. (**13**): ^{1}H NMR δ 7.50-7.26 (m, 10H), 5.62 (s, 1H), 4.89 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 1.2 Hz, 1H), 4.33 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.25-4.16 (m, 2H), 4.09 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.93-3.88 (m, 1H), 3.83-3.66 (m, 5H), 3.01-2.94 (m, 1H), 2.74-2.67 (m, 1H), 2.60 (br.s, 1H), 1.84-1.80 (m, 2H), 1.39 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR : δ137.7, 137.2, 129.2, 128.6, 128.4, 128.2, 128.1, 126.1, 101.8, 92.5, 78.2, 75.8, 74.4, 73.9, 71.0, 70.1, 68.2, 60.9, 44.1, 32.2, 6.1. ESIHRMS Calcd. for $C_{25}H_{32}O_{7Na}S$ $[M+Na]^+$: 499.1766. Found 499.1770. (**14**): ^{1}H NMR δ 7.48-7.26 (m, 10H), 5.63 (s, 1H), 4.89 (dd, *J* = 11.55, 5.1 Hz, 1H), 4.77 (d, *J* = 12 Hz, 1H), 4.58 (s, 1H), 4.41-3.99 (m, 5 H), 3.84-3.57 (m, 3 H), 3.47-3.29 (m, 1H), 2.99-2.94 (m, 1H), 2.74-2.67 (m, 1H), 1.40 (t, *J* = 7.5 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR: δ 137.5, 137.1, 129.3, 128.6, 128.4, 128.2, 128.1, 126.1, 101.8, 92.6, 78.9, 78.3, 76.3, 75.3, 73.9, 70.0, 68.2, 67.2, 64.7, 44.2, 18.2, 6.0. ESIHRMS Calcd. for $C_{25}H_{32}O_7SNa$ $[M+Na]^+$: 499.1766. Found 499.1766.

(+)-(2*S*,3a*R*,8a*S*)-3a-(3-Hydroxypropyl)-1,2-bismethoxycarbonyl-8-phenylsulfonyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3b]indole (11): Hydroboration of (+)-(2*S*,3a*R*,8a*S*)-3a-allyl-1,2-bismethoxycarbonyl-8-phenylsulfonyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3b]indole[3] according to the standard protocol gave the title alcohol. $[\alpha]_D$ = +23° (*c* = 1.1, $CHCl_3$); ^{1}H NMR: δ (50 ^{0}C) 7.97 (d, *J* = 6.9, 3.9 Hz, 2H), 7.55-7.46 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.26-7.19 (m, 1H), 7.08-7.04 (m, 2H), 6.06 (s, 1H), 4.64 (d, *J* = 9.0 Hz, 1H), 3.49 (t, *J* = 6.0 Hz, 2H), 3.35 (br.s, 3H), 3.18 (s, 3H), 2.68 (d, *J* = 12.9 Hz, 1H), 2.35 (dd, *J* = 12.9, 9.3 Hz, 1H), 1.68-1.58 (m, 3H), 1.43 (br.s, 1H), 1.41-1.36 (m, 1H); ^{13}C NMR: δ 171.2, 154.6, 142.8, 134.2, 132.7, 129.3, 129.2, 125.7, 124.4, 124.1, 116.7, 83.4, 62.6, 59.8, 52.3, 52.2, 39.4, 34.8, 27.7. ESIHRMS Calcd. for $C_{23}H_{26}N_2O_7SNa$ $[M+Na]^+$: 497.1358. Found 497.1367.

Typical Procedure for the Reduction of Esters with the Mixture of 1 and 2; 1-Nitro-1-phenyl-4-butanol. To methyl 4-nitro-4-phenylbutanoate (0.036 g, 0.162 mmol) dissolved in a biphasic system of THF (1 mL) and FC-72 (1 mL) was added the 1/1 mixture of **1** and **2** (0.19 g, 0.19 mmol of **2**) followed by stirring for 18 h. After completion, methanol (0.5 mL) was added to quench the excess borane. The fluorous layer was separated and evaporated to give **1** (0.16 g, 84%). The organic layer was concentrated and purified by silica gel column chromatography (hexanes:EtOAc 40:1→ 3:1) to give **1** (0.02 g, 11 %) followed by the title alcohol[4] (0.03 g, 95%).

Typical Procedure for the Reduction of Nitriles with the Mixture of 1 and 2; 2-(2-methylphenyl)ethylamine. To 2-(2-methylphenyl)acetonitrile (0.02 g, 0.15 mmol)

dissolved in THF (1 mL) was added the 1/1 mixture of **1** and **2** (0.18 g, 0.18 mmol of **2**) followed by refluxing for 3 h. The reaction mixture was then cooled to room temperature and 6 N HCl (0.09 mL, 0.54 mmol) was added dropwise. The reaction mixture was then heated under reflux for 0.5 h. The so-formed clear solution was cooled to 0 ^{0}C and FC-72 (1 mL) was added followed by stirring for 1 h. The fluorous phase was then separated and evaporated to give **1** (0.13g, 78%). The organic-aqueous reaction mixture was then basified with 3 M NaOH (0.30 mL, 0.90 mmol) and the liberated amine extracted with ether (5 mL). Concentration of the ether layer followed by column chromatography on silica gel (hexanes:EtOAc 40:1→25:1) gave the fluorous sulfide **1** (0.02 g, 10%) followed by the title amine[5] (0.016 g, 81%).

Typical Procedure for the Reduction of Amides with the Mixture of 1 and 2; *N*-Benzyl-4-hydroxypentylamine. To a solution of *N*-benzyl levulinamide (0.03 g, 0.14 mmol) in a biphasic system of THF (1 mL) and FC-72 (1 mL) was added the 1/1 mixture of **1** and **2** (0.42 g, 0.42 mmol of **2**) followed by refluxing for 4 h. The reaction mixture was then cooled and the fluorous layer evaporated to give **1** (0.33 g, 78%). Methanol (0.5 mL) was added to the organic layer which was then refluxed for 0.5 h. The organics were then concentrated and purified by flash column chromatography on silica gel (hexanes : EtOAc 40:1→1:20) to give the fluorous sulfide **1** (0.03 g, 8%) followed by the title aminoalcohol[4] (0.021 g, 79%).

Typical Procedure for the Oxaborolidine Catalyzed Reduction of Ketones with the Mixture of 1 and 2; (*R*)-(+)-1-phenylethanol: To (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (0.004 g, 0.0150 mmol) dissolved in a biphasic system of THF (0.5 mL) and FC-72 (0.5 mL) was added the 1/1 mixture of **1** and **2** (0.30 g, 0.30 mmol of **2**) followed by stirring at 45 ^{0}C overnight. Acetophenone (0.018 g, 0.150 mmol) was then added dropwise over a period of 30 min. After stirring for an additional 30 min the reaction mixture was quenched with methanol (0.3 mL). The fluorous layer was separated and the organic layer was then stirred with additional FC-72 (1 mL). The fluorous layers were combined and concentrated to give **1** (0.24 g, 80 The organics were concentrated and purified by column chromatography on silica gel (hexanes:EtOAc 40:1→1:20) to give the fluorous sulfide **1** (0.04 g, 12%) followed by (*R*)-(+)-1-phenylethanol (0.017g, 94%). $[\alpha]_D = +40^{\circ}$ (*c*, 0.4g, CH_2Cl_2, 84% ee)

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