

## The Regioselectivity of Addition of Organolithium

### Reagents to Enones: The Role of HMPA

Hans J. Reich\* and William H. Sikorski

Department of Chemistry, University of Wisconsin

Madison, Wisconsin 53706

### Supplementary Material

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NOV 16 1998

Journal of Organic Chemistry

## Experimental

**General.** Tetrahydrofuran (THF) and Et<sub>2</sub>O were freshly distilled from sodium benzophenone ketyl before use. Hexamethylphosphoramide (HMPA) was distilled from CaH<sub>2</sub> at reduced pressure and stored under N<sub>2</sub> over molecular sieves. Glassware was placed overnight in a 110 °C oven or flame-dried before purging with N<sub>2</sub> to remove moisture. Common lithium reagents were titrated using *n*-propanol in THF with 1,10-phenanthroline as an indicator.<sup>[1]</sup> Temperatures of -78 °C were achieved with a dry ice/acetone bath, -120 °C with an LN<sub>2</sub> / pentane bath, and -20 °C with a chemical freezer. Melting and boiling points are not corrected. Kugelrohr distillation temperatures refer to the pot temperature.

Commercially available starting materials and reagents (obtained from Aldrich Chemical Company) include: *bis*(phenylthio)methane (**3-H**), 3,5-*bis*(trifluoromethyl)bromobenzene, *t*-butyl mercaptan, chloromethyl methyl sulfide (CH<sub>3</sub>SCH<sub>2</sub>Cl),  $\alpha$ -chloro-*m*-xylene, 2-cyclohexen-1-one (**2**), hexamethylphosphoramide (HMPA), 2-methyl-1,3-dithiane (**5-H**), thiophenol (PhSH), and triethylamine (Et<sub>3</sub>N).

## Syntheses

***t*-Butylthio(methylthio)methane (4-H).** To a dried, N<sub>2</sub>-purged, 50 mL rb flask with stir bar, which was fitted with a septum and maintained under positive N<sub>2</sub> pressure, was added 26.8 mL (39.9 mmol) of 1.49 M MeLi in Et<sub>2</sub>O. The solution was cooled to -78 °C and *t*-butyl mercaptan (3.6 g, 39.9 mmol) was added dropwise followed by 3.86 g (40.0 mmol) of CH<sub>3</sub>SCH<sub>2</sub>Cl. The cold bath was removed, and the solution was allowed to warm to room temperature and stir for 3 hours. The

contents were transferred to a separatory funnel, 25 mL of hexane was added, and the solution was washed with 3 x 30 mL of 10% NaOH, 30 mL of H<sub>2</sub>O, and 30 mL of brine and dried over anhydrous MgSO<sub>4</sub>. The solvents were removed by rotary evaporation, and the product was fractionally distilled (110 °C at 50 mm Hg) to yield 1.77 g (11.8 mmol, 29.4%) of a colorless liquid. Density = 0.9580 g / mL. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.37 (CH<sub>3</sub>, s, 9H), 2.21 (CH<sub>3</sub>, s, 3H), 3.68 (CH<sub>2</sub>, s, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 15.20 (SCH<sub>3</sub>), 30.81 (CH<sub>3</sub>), 33.87 (CH<sub>2</sub>), 43.27 (C). The spectroscopic results agree with literature data.<sup>[2]</sup>

**3,5-Bis(Trifluoromethyl)thiophenol.** CAUTION: *This synthesis involves the formation of a trifluoromethyl-substituted aryllithium. While they appear to be stable in solution, there are several reports of explosions when the solvent was removed from such compounds (and their Grignard counterparts).<sup>[4]</sup> This class of organometallic reagents should not be purified.*

To a dried, N<sub>2</sub>-purged, 500 mL rb flask with stir bar, which was fitted with a septum and maintained under positive N<sub>2</sub> pressure, were added 3,5-bis(trifluoromethyl)bromobenzene (20.4 g, 69.6 mmol) and Et<sub>2</sub>O (300 mL). The solution was cooled to -120 °C using an LN<sub>2</sub> / pentane bath. To the solution were added via cannula 76 mL (139.2 mmol) of 1.83 M *t*-BuLi in pentane, dropwise along the inside of the flask (to cool and disperse it). The entire addition required 25 minutes, over which time the solution became cloudy and yellow. *It is essential that the addition be performed slowly so that the low temperature can be maintained, otherwise decomposition occurs and the solution turns black.* The septum was removed briefly, and 2.23 g (69.6 mmol) of elemental sulfur was added rapidly. The solution was stirred at this low temperature for an additional 10 minutes, dry ice was added to the pentane bath, and the solution was allowed to gradually warm to -78 °C. After 45 minutes, the solution was clear and no more sulfur was visible. The reaction was quenched (dropwise initially — exothermic!) with 20 mL of H<sub>2</sub>O followed by 50 mL of 6N HCl, and the solution was allowed to warm to room temperature. The organic layer was separated, washed with 2 x 100 mL portions of H<sub>2</sub>O and 100 mL of brine, and dried over anhydrous MgSO<sub>4</sub>. The solvents were removed by rotary evaporation and the residue was distilled (93 °C @ 24 mm Hg), yielding 5.00 g (20.3 mmol, 29.2 %) of a clear, colorless, foul-smelling liquid (an aggressive lachrymator). Note:

the compound freezes slightly below room temperature, and some of the compound froze in the condenser tube and had to be allowed to melt to be collected.

The residue in the distillation pot (largely the disulfide) was reduced to the thiol by adding 10 mL of glacial acetic acid and 5 g of zinc dust and heating to 100 °C for 1 hour. After adding 40 mL of 6N HCl, the solution was allowed to cool to room temperature. The zinc was removed using a fritted glass funnel and rinsed with 2 x 25 mL of Et<sub>2</sub>O. The organic layer was separated and washed with 2 x 25 mL of H<sub>2</sub>O and 25 mL of brine. The solution was dried with anhydrous MgSO<sub>4</sub>, concentrated by rotary evaporation, and distilled as before, yielding an additional 3.2 g (total yield 8.2 g, 33.3 mmol, 47.9 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.75 (SH, s), 7.64 (Ar-4, broad s), 7.68 (Ar-2&6, broad s). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 119.44 (Ar-4, sept, <sup>3</sup>J<sub>C-F</sub> = 3.50 Hz), 122.93 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>C-F</sub> = 272.96 Hz), 128.75 (Ar-2&6, broad q, <sup>3</sup>J<sub>C-F</sub> not resolved), 132.45 (Ar-3&5, q, <sup>2</sup>J<sub>C-F</sub> = 33.70 Hz), 134.87 (Ar-1). Mass Spec: M<sup>+</sup> = 245.9944 (calc. for C<sub>8</sub>H<sub>4</sub>F<sub>6</sub>S = 245.9938).

**Bis[3,5-Bis(Trifluoromethyl)phenylthio]methane (6-H).** To a 100 mL rb flask with stir bar were added 50 mL of MeCN, 2.49 g (10.1 mmol) of 3,5-bis(trifluoromethyl)thiophenol, 0.41 mL (5.09 mmol) of CH<sub>2</sub>Cl<sub>2</sub>, and 1.02 g (10.1 mmol) of Et<sub>3</sub>N (turning the solution intensely yellow). Over the next 10 minutes, most of the yellow color had dissipated, but the solution was allowed to stir for a total of 2 hours. The solvent was removed by rotary evaporation and replaced with 100 mL of 1:1 Et<sub>2</sub>O/hexane. The solution was washed with 2 x 50 mL of 10% NaOH, 50 mL of H<sub>2</sub>O, and 50 mL of brine and dried over anhydrous MgSO<sub>4</sub>. The solvents were removed by rotary evaporation, and the residue was taken up in boiling hexane and allowed to crystallize at -20 °C. Two additional crops were isolated from the mother liquor, yielding a total of 1.71 g (3.39 mmol, 67.1%). MP: 32.0-32.5 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.49 (CH<sub>2</sub>, s, 2H), 7.76 (Ar-CH, broad s, 2H), 7.78 (Ar-CH, broad s, 4H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 39.49 (CH<sub>2</sub>), 121.31 (Ar-4, sept, <sup>3</sup>J<sub>C-F</sub> = 3.81 Hz), 122.81 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>C-F</sub> = 273.39 Hz), 130.28 (Ar-2&6, broad q, <sup>3</sup>J<sub>C-F</sub> not resolved), 132.55 (Ar-3&5, q, <sup>2</sup>J<sub>C-F</sub> = 33.70 Hz), 137.26 (Ar-1). MS: M<sup>+</sup> = 503.9888 (calc. for C<sub>17</sub>H<sub>8</sub>S<sub>2</sub>F<sub>12</sub> = 503.9876).

**3-Methylbenzyl Phenyl Sulfide (7-H).** To a 250 mL rb flask with stir bar were added 125 mL of MeCN, 5.32 g (37.8 mmol) of α-chloro-*m*-xylene, and 4.18 g (38.0 mmol) of PhSH. With vigorous stirring, 3.85 g (38 mmol) of Et<sub>3</sub>N was added dropwise, producing Et<sub>3</sub>N·HCl. The solid was

filtered away using a fritted glass funnel, and the solid was rinsed with an addition 50 mL of MeCN. The solution was concentrated by rotary evaporation, taken up in 100 mL of 1:1 Et<sub>2</sub>O/hexane, and washed with 2 x 50 mL of 10% NaOH, 50 mL of H<sub>2</sub>O, and 50 mL of brine. The solution was dried over anhydrous MgSO<sub>4</sub>, the solvents were removed by rotary evaporation, and the product was distilled (109-110 °C @ 0.02 mm Hg), yielding 5.19 g (24.2 mmol, 64.1 %) of a pale yellow liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.29 (CH<sub>3</sub>, s), 4.06 (CH<sub>2</sub>, s), 7.00-7.33 (Ar, m, 9H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 21.29 (CH<sub>3</sub>), 38.88 (CH<sub>2</sub>), 125.80 (CH), 126.16 (CH), 127.90 (CH), 128.31 (CH), 128.75 (CH), 129.52 (CH), 129.56 (CH), 136.57 (C), 137.18 (C), 138.07 (C). Mass Spec: M<sup>+</sup> = 214.0819 (calc. for C<sub>14</sub>H<sub>14</sub>S = 214.0816).

**5-Trimethylsilyl-2-cyclohexen-1-one (8).** This compound was synthesized according to a literature procedure.<sup>[3]</sup> The product was distilled (60-63 °C @ 1 mm Hg, lit. 65.5-67 °C @ 2.0 mm Hg). Density: 0.9020 g/mL. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.22 (CH<sub>3</sub>, s, 9H), 1.18 (H<sub>5</sub>, dddd, <sup>3</sup>J<sub>5-6a</sub> = 14.89 Hz, <sup>3</sup>J<sub>5-4a</sub> = 11.58 Hz, <sup>3</sup>J<sub>5-4e</sub> = 4.78 Hz, <sup>3</sup>J<sub>5-6e</sub> = 3.86 Hz), 1.94 (H<sub>4a</sub>, ddt, <sup>2</sup>J<sub>4a-4e</sub> = 18.94 Hz, <sup>3</sup>J<sub>4a-5</sub> = 11.40 Hz, <sup>3</sup>J<sub>4a-3</sub> = <sup>4</sup>J<sub>4a-2</sub> = 2.57 Hz), 1.96 (H<sub>6a</sub>, dd, <sup>2</sup>J<sub>6a-6e</sub> = 16.55 Hz, <sup>3</sup>J<sub>6a-5</sub> = 14.52 Hz), 2.08 (H<sub>4e</sub>, dtt, <sup>2</sup>J<sub>4e-4a</sub> = 19.12 Hz, <sup>3</sup>J<sub>4e-3e</sub> = <sup>3</sup>J<sub>4e-5</sub> = 5.15 Hz, <sup>4</sup>J<sub>4e-2</sub> = <sup>4</sup>J<sub>4e-6e</sub> = 1.29 Hz), 2.17 (H<sub>6e</sub>, ddt, <sup>2</sup>J<sub>6e-6a</sub> = 16.36 Hz, <sup>3</sup>J<sub>6e-5</sub> = 3.86 Hz, <sup>4</sup>J<sub>6e-2</sub> = <sup>4</sup>J<sub>6e-4e</sub> = 1.10 Hz), 5.74 (H<sub>2</sub>, ddt, <sup>3</sup>J<sub>2-3</sub> = 9.84 Hz, <sup>4</sup>J<sub>2-4a</sub> = 2.76 Hz, <sup>4</sup>J<sub>2-4e</sub> = <sup>4</sup>J<sub>2-6e</sub> = 1.10 Hz), 6.79 (H<sub>3</sub>, <sup>3</sup>J<sub>3-2</sub> = 10.11 Hz, <sup>3</sup>J<sub>3-4e</sub> = 5.52 Hz, <sup>3</sup>J<sub>3-4a</sub> = 2.57 Hz). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ -3.91 (CH<sub>3</sub>), 22.98 (CH), 26.61 (CH<sub>2</sub>), 38.45 (CH<sub>2</sub>), 129.23 (CH), 151.20 (CH), 199.81 (C).

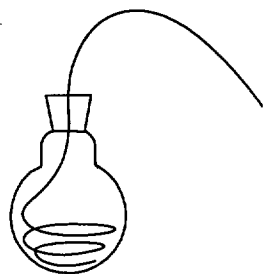
## Enone Trapping Studies

All of the enone trapping studies were performed using the same procedure, which is written out in detail here for the reaction between *bis*(phenylthio)methyl lithium (3) and 2-cyclohexen-1-one (2). The specific details for the other systems follow.

### *Bis*(Phenylthio)methyl lithium (3) and 2-Cyclohexen-1-one (2)

A 10 mL round-bottom flask was prepared in advance with one end of a cannula coiled inside. We have found that the easiest and most reliable method of coiling the cannula inside the flask is to first heat the portion of the cannula to be shaped in a flame until it glows. This changes the properties of the metal, and, upon cooling, the metal is very pliable. The softened portion of the cannula is

wrapped about a tube of sufficient diameter to form the proper coil size (which should be large enough to allow a stir bar to spin freely within). The handedness of the coil should be made to be opposite of the motion of the stir bar, to maximize agitation at the opening of the cannula. The cannula is slid off of the tube, and the two ends of the cannula are pulled in opposite directions to draw out the coil. The cannula is fed straight into the flask, and when the tip of the cannula pushes against the bottom of the flask, it regains the coiled shape. The coil is placed low enough to be submerged in the liquid in the flask, so that the solution being added via the cannula will be cooled before exiting the cannula (heat transfer through the thin metal of the cannula is very efficient). The cannula length should be as short as possible to accomplish the task described below, to minimize warming of the solution being introduced through it.



The flask (with cannula and stir bar) was dried overnight in an oven. The external end of the cannula was poked through the bottom of a septum, and the septum was passed along it into position. An  $N_2$  inlet needle was introduced into the flask, purging the flask and the cannula. When purging was complete, the free end of the cannula was plugged by imbedding it into a thick piece of septum.

The flask was charged with 1.8 mL of THF, 1.2 mL of  $Et_2O$ , 58 mg (0.25 mmol) of **3-H**, and the necessary amount of HMPA (1 equiv. = 43.5  $\mu L$ ). The flask was cooled to  $-78^\circ C$  under positive  $N_2$  pressure, and 0.125 mL (0.25 mmol) of 2.0 M *n*-BuLi in pentane was added.

A dried,  $N_2$ -purged, 5 mL conical flask fitted with a septum was charged with 0.6 mL of THF, 0.4 mL of  $Et_2O$ , and 12.0  $\mu L$  (11.9 mg, 0.124 mmol, 0.50 equiv.) of **2**, and both flasks were cooled under positive  $N_2$  pressure to  $-120^\circ C$  using an  $N_{2(l)}$  / pentane slurry.

An  $N_2$  inlet needle was introduced into the conical flask containing **2** and turned on momentarily to build up pressure. The septum plug was removed from the exposed end of the cannula, and the

cannula was immediately inserted into the conical flask, with the N<sub>2</sub> pressure inside being dissipated through the cannula, purging it of any liquids and preventing a back flow. The N<sub>2</sub> gas through the inlet needle was again turned on, the end of the cannula was submerged in the liquid, transferring it to the anion over the course of approximately 5 sec. (occasionally an experiment had to be abandoned due to a plugged cannula).

After 1 min. at this temperature, 3 mL (0.8 mmol) of 0.27 M propionic acid/Et<sub>2</sub>O (1:49), which is a protic quench that does not freeze at these temperatures, was added via syringe. The solution was allowed to warm to room temperature, the contents were transferred to a separatory funnel, and 20 mL of 1:1 Et<sub>2</sub>O/hexane was added. The solution was washed with 3 x 20 mL of H<sub>2</sub>O, dried over anhydrous MgSO<sub>4</sub>, and concentrated by rotary evaporation.

The ratios of products were determined by <sup>1</sup>H NMR integration with C<sub>6</sub>D<sub>6</sub> as solvent (300 MHz spectrometer), using the proton on the *bis*(sulfur)-substituted carbon: starting material = δ 3.98 (s, 2H); 1,2 product = δ 4.61 (s, 1H); and 1,4 product = δ 4.29 (d, J = 3.60 Hz, 1H). Although, in general, a relaxation delay was not used during the NMR acquisitions, occasionally the reliability of the integrations was checked by introducing delays of up to 20 s, which, without exception, had absolutely no effect on either the ratio of the two products or their ratios to the returned starting material. For characterization, the addition products were isolated by preparative TLC.

**1-[Bis(Phenylthio)methyl]-2-cyclohexen-1-ol:** R<sub>f</sub> (20% EtOAc/hexane): 0.38. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.63-2.16 (CH<sub>2</sub>, m, 6H), 2.80 (OH, broad s, 1H), 4.47 (S-CH-S, s, 1H), 5.76 (=CH, ddt, J = 9.93, 2.39, 1.65 Hz, 1H), 5.97 (=CH, dddd, J = 10.10, 4.60, 2.02, 0.74 Hz, 1H), 7.14-7.36 (Ph, m, 10H). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.43-1.53 (m, 1H), 1.72-1.91 (m, 3H), 1.92-2.01 (m, 1H), 2.11-2.23 (m, 1H), 2.68 (OH, broad s, 1H), 4.61 (S-CH-S, s, 1H), 5.73-5.81 (=C<sup>3</sup>H, m, 1H), 5.88-5.94 (C<sup>2</sup>H=, m, 1H), 6.87-6.97 (Ph, m, 6H), 7.29-7.39 (Ph, m, 4H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 18.56 (CH<sub>2</sub>), 25.09 (CH<sub>2</sub>), 33.18 (CH<sub>2</sub>), 72.88 (C-OH), 74.18 (S-CH-S), 127.57 (CH), 127.59 (CH), 128.76 (CH), 128.81 (CH), 129.17 (=CH), 132.63 (CH), 132.65 (=CH), 132.87 (CH), 134.94 (C), 134.99 (C). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 19.04 (CH<sub>2</sub>), 25.45 (CH<sub>2</sub>), 33.78 (CH<sub>2</sub>), 73.18 (COH), 74.76 (S-CH-S), 127.62 (CH), 129.04 (CH), 129.09 (CH), 130.23 (=CH), 132.16

(=CH), 133.01 (CH), 133.13 (CH), 136.04 (C), 136.14 (C). IR (neat): 3462  $\text{cm}^{-1}$  (OH), lit.<sup>[5]</sup> 3400  $\text{cm}^{-1}$ . MS:  $M^+ = 328.0957$  (calc. for  $\text{C}_{19}\text{H}_{20}\text{OS}_2 = 328.09556$ ).

**3-[Bis(Phenylthio)methyl]cyclohexanone:**  $R_f$  (20% EtOAc/hexane): 0.45.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.45-1.63 (m, 1H), 1.66-1.83 (m, 1H), 2.04-2.42 (m, 5H), 2.53 ( $\text{H}_{2\text{-eq}}$ , ddt,  $J = 13.79$ , 4.23, 2.02 Hz, 1H), 2.63 ( $\text{H}_{2\text{-ax}}$ , ddd,  $J = 13.97$ , 12.50, 0.92 Hz, 1H), 4.34 (S-CH-S, d,  $J = 3.49$  Hz, 1H), 7.24-7.31 (Ph, m, 6H), 7.35-7.43 (Ph, m, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.57 ( $\text{CH}_2$ ), 27.38 ( $\text{CH}_2$ ), 41.05 ( $\text{CH}_2$ ), 43.38 (CH), 45.09 ( $\text{CH}_2$ ), 65.49 (S-CH-S), 127.84 (CH), 127.91 (CH), 129.04 (CH), 132.47 (CH), 132.65 (CH), 134.34 (C), 134.47 (C), 210.41 (C=O). IR (neat): 1711  $\text{cm}^{-1}$  (C=O), lit.<sup>[5]</sup> 1710  $\text{cm}^{-1}$ . MS:  $M^+ = 328.0957$  (calc. for  $\text{C}_{19}\text{H}_{20}\text{OS}_2 = 328.09556$ ).

***t*-Butylthio(methylthio)methylithium (4) and 2-Cyclohexen-1-one (2).** The general procedure was used with the following changes: 39.2  $\mu\text{L}$  (37.6 mg, 0.25 mmol) of 4-H was used and, after the addition of *n*-BuLi (still at  $-78^\circ\text{C}$ ), the solution was warmed to room temperature for 15 min. to complete the metallation before cooling to  $-120^\circ\text{C}$ . Product ratios were determined using the following  $^1\text{H}$  NMR signals in  $\text{C}_6\text{D}_6$ : starting material =  $\delta$  3.43 (s, 2H); 1,2 diastereomers =  $\delta$  3.71 (s, 1H), 3.7 (s, 1H); 1,4 diastereomers =  $\delta$  3.35 (d,  $J = 3.6$  Hz, 1H), 3.40 (d,  $J = 3.4$  Hz, 1H).

**2-Methyl-1,3-dithianyllithium (5) and 2-Cyclohexen-1-one (2).** The general procedure was used with the following changes. A stock solution of 5 was prepared by dissolving 0.24 mL (0.27 g, 2.0 mmol) of 5-H in 18.6 mL of THF and 12.4 mL of  $\text{Et}_2\text{O}$ , cooling to  $-78^\circ\text{C}$ , adding 0.95 mL (2.02 mmol) of 2.13 M *n*-BuLi in pentane, and storing overnight at  $-20^\circ\text{C}$  (the resulting solution, 0.0626 M in 5, is good for about one week at  $-20^\circ\text{C}$ ). A syringe was used to transfer 4.0 mL (0.25 mmol of 5) to the flask containing the cannula. Product ratios were determined using the following  $^1\text{H}$  NMR signals in  $\text{C}_6\text{D}_6$ : starting material =  $\delta$  3.81 (CH, q,  $J = 6.99$  Hz, 1H); 1,2 product =  $\delta$  6.32 (=CH, dq,  $J = 10.29$ , 1.78 Hz, 1H); and 1,4 product =  $\delta$  2.96 (CH, dq,  $J = 12.87$ , 2.45 Hz, 1H).

**1-[2-(2-Methyl-1,3-dithianyl)]-2-cyclohexen-1-ol:**  $R_f$  (20% EtOAc/hexane): 0.32.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.70-2.10 (m, 8H), 1.77 ( $\text{CH}_3$ , s, 3H), 2.28 (OH, s, 1H), 2.88-2.98 (m, 4H), 5.97-6.05 (=CH, m, 1H), 6.10-6.17 (=CH, m, 1H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.83 ( $\text{CH}_2$ ), 24.31 ( $\text{CH}_3$ ), 25.00 ( $\text{CH}_2$ ), 25.13 ( $\text{CH}_2$ ), 26.69 ( $\text{CH}_2$ ), 26.82 ( $\text{CH}_2$ ), 31.01 ( $\text{CH}_2$ ), 59.44 ( $\text{S}_2\text{C}$ ), 75.62

(COH), 128.35 (=CH), 132.84 (=CH). IR (neat): 3466  $\text{cm}^{-1}$  (OH). MS:  $M^+ = 230.0793$  (calc. for  $\text{C}_{11}\text{H}_{18}\text{OS}_2 = 230.07991$ ).

**3-[2-(2-Methyl-1,3-dithianyl)]cyclohexanone:**  $R_f$  (20% EtOAc/hexane): 0.41.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.50-1.70 (m, 2H), 1.62 (OH, s, 1H), 1.90-2.03 (m, 2H), 2.10-2.45 (m, 6H), 2.77-2.90 (m, 5H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.40 ( $\text{CH}_3$ ), 24.84 ( $\text{CH}_2$ ), 25.06 ( $\text{CH}_2$ ), 26.07 ( $\text{CH}_2$ ), 26.21 ( $\text{CH}_2$ ), 26.29 ( $\text{CH}_2$ ), 41.09 ( $\text{CH}_2$ ), 43.08 ( $\text{CH}_2$ ), 46.27 (CH), 52.50 ( $\text{S}_2\text{C}$ ), 211.34 (C=O). IR (neat): 1708  $\text{cm}^{-1}$  (C=O). MS:  $M^+ = 230.0804$  (calc. for  $\text{C}_{11}\text{H}_{18}\text{OS}_2 = 230.07991$ ).

**Bis[3,5-Bis(Trifluoromethyl)phenylthio]methylithium(6) and 2-Cyclohexen-1-one (2).** The general procedure was used with the following changes: 126 mg (0.25 mmol) of *bis*[3,5-*bis*(trifluoromethyl)phenylthio)methane (6-H) was used; and, for experiments with greater than 1 equiv. of HMPA, a reaction time of 1 hour was used. Product ratios were determined using the following  $^1\text{H}$  NMR signals in  $\text{C}_6\text{D}_6$ : starting material =  $\delta$  3.28 (s, 2H); 1,2 product =  $\delta$  4.40 (s, 1H); and 1,4 product =  $\delta$  4.15 (d,  $J = 3.90$  Hz, 1H).

**1-{Bis[3,5-Bis(Trifluoromethyl)phenylthio]methyl}-2-cyclohexen-1-ol:**  $R_f$  (20% EtOAc/hexane): 0.60.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.78-1.93 (m, 2H), 2.00-2.26 (m, 4H), 2.49 (OH, s, 1H), 4.62 (S-CH-S, s, 1H), 5.86 (=CH, ddt,  $J = 10.11, 2.57, 1.47$  Hz, 1H), 6.12 (=CH, ddd,  $J = 9.93, 4.96, 2.57$  Hz, 1H), 7.67-7.72 (Ar, m, 6H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.62 ( $\text{CH}_2$ ), 25.14 ( $\text{CH}_2$ ), 33.60 ( $\text{CH}_2$ ), 72.50 (CH), 72.77 (C), 121.37 (Ar-4, sept,  $^3J_{\text{C-F}} = 3.18$  Hz), 121.59 (Ar-4', sept,  $^3J_{\text{C-F}} = 3.18$  Hz), 122.66 ( $\text{CF}_3$ , q,  $^1J_{\text{C-F}} = 273.39$  Hz), 128.38 (=CH), 131.21 (Ar-2, q,  $^3J_{\text{C-F}}$  not resolved), 132.04 (Ar-2', q,  $^3J_{\text{C-F}}$  not resolved), 134.49 (=CH), 137.77 (C), 138.19 (C). IR ( $\text{CCl}_4$ ): 3443  $\text{cm}^{-1}$  (OH). MS:  $M^+ = 600.0495$  (calc. for  $\text{C}_{23}\text{H}_{16}\text{OS}_2\text{F}_{12} = 600.04512$ ).

**3-{Bis[3,5-Bis(Trifluoromethyl)phenylthio]methyl}cyclohexanone:**  $R_f$  (20% EtOAc/hexane): 0.54.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.60-1.90 (m, 2H), 2.00-2.53 (m, 5H), 2.65-2.74 (m, 2H), 4.61 (S-CH-S, d,  $J = 3.86$  Hz), 7.67-7.75 (Ar, m, 6H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.42 ( $\text{CH}_2$ ), 28.24 ( $\text{CH}_2$ ), 40.89 ( $\text{CH}_2$ ), 44.07 (CH), 45.09 ( $\text{CH}_2$ ), 66.17 (S-CH-S), 121.96 (Ar-4, sept,  $^3J_{\text{C-F}} = 3.50$  Hz), 122.12 (Ar-4', sept,  $^3J_{\text{C-F}} = 3.50$  Hz), 122.58 ( $\text{CF}_3$ , q,  $^1J_{\text{C-F}} = 272.75$  Hz), 131.83 (Ar-2, broad q,  $^3J_{\text{C-F}}$  not resolved), 132.28 (Ar-2', broad q,  $^3J_{\text{C-F}}$  not resolved), 132.55 (Ar-3, q,  $^2J_{\text{C-F}} = 34.33$  Hz),

136.81 (Ar-1), 137.02 (Ar-1'), 208.76 (C=O). IR (CCl<sub>4</sub>): 1716 cm<sup>-1</sup> (C=O). MS: M<sup>+</sup> = 600.0446 (calc. for C<sub>23</sub>H<sub>16</sub>OS<sub>2</sub>F<sub>12</sub> = 600.04512).

**Rate of Reaction of Bis[3,5-Bis(Trifluoromethyl)phenylthio]methylithium(6) with 2-Cyclohexen-1-one (2).** To an oven-dried nitrogen purged 5 mL long-necked round-bottom flask fitted with a septum and stirbar was added 0.126 g (0.25 mmol) of 6-H, 1.8 mL of THF and 1.2 mL of ether. The flask was cooled to -78 °C, and 0.13 mL of 1.97 M nBuLi (0.25 mmol) was added *slowly*, with vigorous stirring, down the side of the flask to ensure cooling of the nBuLi solution. The solution becomes dark orange. The flask was cooled to -120 °C (LN<sub>2</sub>-pentane), and a solution of 24 μL (0.25 mmol) of cyclohexenone in 0.4 mL of ether and 0.6 mL of THF, precooled to -78 °C, was transferred to the solution of 6. The reaction mixture was vigorously stirred for 30 sec, and rapidly quenched with 2 mL of 0.27 M propionic acid in THF. Workup as usual and analysis by <sup>1</sup>H NMR (vs pentachloroethane internal standard) showed a 94% recovery, 34% conversion and a 1.43:1 ratio of 1,2- to 1,4-addition products. A pseudo-first-order rate constant of 1.4x10<sup>-2</sup> sec<sup>-1</sup> was calculated from the percent reaction.

A identical experiment except that 174 μL (179 mg, 1 mmol) of HMPA was added to the solution of 6, and a reaction time of 1 h was used, gave 84% recovery, 2.7% reaction (integration vs <sup>13</sup>C satellite of 6-H) and a 1: 4 ratio of 1,2- to 1,4-addition products. A pseudo-first-order rate constant of 7.7x10<sup>-6</sup> sec<sup>-1</sup> was calculated from the percent reaction. Thus  $k_{\text{THF}}/k_{\text{THF-HMPA}} = 1820$ .

**Phenylthio(3-methyl)benzylithium (7) and 5-Trimethylsilyl-2-cyclohexen-1-one (8): HMPA Dependence in Et<sub>2</sub>O (with 90 equiv. of THF) at -120 °C.** The general procedure was used with the following changes: 49.0 μL (52.7 mg, 0.25 mmol) of 7-H and 46.6 μL (42.0 mg, 0.25 mmol) of 8 were used. Different NMR solvents needed to be used to determine the ratios of the 1,2 and 1,4 products, due to coincident signals. The 1,4 product ratios were determined using <sup>1</sup>H NMR signals in CDCl<sub>3</sub>: starting material = δ 4.04, s, 2H; 1,4 diastereomers = δ 3.85 (d, J = 10.3 Hz, 1H), 3.9 (d, J = 10.7 Hz, 1H), 4.00 (d, J = 7.0 Hz, 1H), 4.09 (d, J = 5.9 Hz, 1H); 1,2 diastereomers = δ 4.17 (two coincident signals), 4.25, 4.39. The 1,2 product ratios were determined using <sup>1</sup>H NMR signals in C<sub>6</sub>D<sub>6</sub>: starting material = δ 3.82 (s, 2H); 1,2 diastereomers = δ 4.21 (s, 1H), 4.29 (s, 1H), 4.38 (s,

1H), 4.44 (s, 1H); 1,4 diastereomers =  $\delta$  3.87 (d, J = 10.8 Hz), 3.90 (two coincident signals, d, J = 6.6 Hz), 4.10 (d, J = 10.5 Hz).

**1-[Phenylthio(3-methyl)benzyl]-5-(trimethylsilyl)-2-cyclohexen-1-ol** (diastereomers A, B, C and D):  $R_f$  (20% EtOAc/hexane): 0.56.  $^1\text{H NMR}$  (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -0.23 ( $\text{SiMe}_3$  A), -0.13 ( $\text{SiMe}_3$  D), -0.11 ( $\text{SiMe}_3$  C), -0.10 ( $\text{SiMe}_3$  B), 0.60-1.90 (m, 6H), 2.00-2.35 (m, 4H), 2.69 (B, dm, J = 13.60 Hz), 4.21 (SCH D), 4.29 (SCH C), 4.38 (SCH B), 4.43 (SCH A), 5.39 (=CH B, dm, J = 10.30 Hz), 5.56 (=CH B, ddd, J = 10.1, 4.4, 2.8 Hz), 5.68 (=CH A, ddd, J = 10.1, 4.4, 2.4 Hz), 5.78-5.94 (=CH, m, 1H), 6.33 (=CH D, dm, J = 10.11 Hz), 6.46 (=CH A, dm, J = 10.11 Hz), 6.78-6.94 (m, 4H), 7.00-7.10 (m, 1H), 7.28-7.40 (m, 4H).  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -3.89 ( $\text{SiMe}_3$  A), -3.71 ( $\text{SiMe}_3$  D), -3.68 ( $\text{SiMe}_3$  C), 16.85 (C or D), 16.90 (C or D), 18.92 (A), 19.49 (B), 21.39, 25.99 ( $\text{CH}_2$  B), 26.20 ( $\text{CH}_2$  A), 26.44 ( $\text{CH}_2$  C), 26.49 ( $\text{CH}_2$  D), 35.89 ( $\text{CH}_2$  A), 35.93 ( $\text{CH}_2$  C), 35.99 ( $\text{CH}_2$  D), 36.51 ( $\text{CH}_2$  B), 64.83 (SCH A), 65.51 (SCH B), 65.83 (SCH D), 66.93 (SCH C), 71.19 (COH D), 71.57 (COH C), 73.50 (COH A), 73.54 (COH B), 126.57 (CH), 126.77 (CH), 126.81 (CH), 126.98 (CH), 127.26 (CH), 127.33 (CH), 127.48 (CH), 127.97 (CH), 128.09 (CH), 128.11 (CH), 128.17 (CH), 128.28 (CH), 128.65 (CH), 128.89 (CH), 128.97 (CH), 129.01 (CH), 129.61 (CH), 130.46 (CH), 130.52 (CH), 130.74 (CH), 130.84 (CH), 130.90 (CH), 131.03 (CH), 131.17 (CH), 131.74 (CH), 132.08 (CH), 132.11 (CH), 132.47 (CH), 132.91 (CH), 134.77 (CH), 136.98 (C), 137.11 (C), 137.22 (C), 137.41 (C), 137.46 (C), 137.54 (C), 140.12 (C), 140.33 (C), 140.93 (C), 140.95 (C). IR (neat): 3456  $\text{cm}^{-1}$  (OH), 3541  $\text{cm}^{-1}$  (OH). MS:  $M^+ = 382.1781$  (calc. for  $\text{C}_{23}\text{H}_{30}\text{OSSi} = 382.1787$ ).

**3-[Phenylthio(3-methyl)benzyl]-5-trimethylsilylcyclohexanone** (diastereomers A, B, C and D):  $R_f$  (20% EtOAc/hexane): 0.44.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.22 ( $\text{SiMe}_3$  D), -0.07 ( $\text{SiMe}_3$  A), -0.02 ( $\text{SiMe}_3$  B or C), 0.01 ( $\text{SiMe}_3$  B or C), 0.85-1.63 (m, 2H), 1.75-3.06 (m, 9 H), 3.85 (SCH D, d, J = 10.30 Hz), 3.95 (SCH C, d, J = 10.67 Hz), 4.00 (SCH B, d, J = 6.99 Hz), 4.09 (SCH A, d, J = 5.88 Hz).  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  -3.83 ( $\text{SiCH}_3$  A), -3.77 ( $\text{SiCH}_3$  D), -3.46 ( $\text{SiCH}_3$  B or C), 21.16 (B or C), 21.25 (D), 21.33 (A), 25.62, 25.68, 28.42 ( $\text{CH}_2$  D), 28.83 ( $\text{CH}_2$  B or C), 29.81 ( $\text{CH}_2$  A), 30.69 ( $\text{CH}_2$  B or C), 41.64 ( $\text{CH}_2$  B or C), 41.73 ( $\text{CH}_2$  A), 41.92 ( $\text{CH}_2$  B or C), 41.98 ( $\text{CH}_2$  D), 42.57 (CH D), 42.90 (CH B or C), 44.38 ( $\text{CH}_2$  B or C), 44.94 ( $\text{CH}_2$  D), 45.72 ( $\text{CH}_2$  A), 46.02

(CH<sub>2</sub> B or C), 47.37 (CH A), 47.49 (CH B or C), 56.93 (SCH B or C), 57.71 (SCH D), 59.31 (SCH A), 59.96 (SCH B or C), 125.07 (CH D), 125.33 (CH B or C), 125.46 (CH A), 126.79 (CH A), 126.85 (CH B or C), 127.07 (CH B or C), 127.19 (CH D), 127.73 (CH D), 127.81 (CH B or C), 127.98 (CH A), 128.03 (CH D), 128.08 (CH B or C), 128.50 (CH A), 128.61 (CH D), 128.67 (CH A), 128.78 (CH B or C), 128.95 (CH B or C), 129.03 (CH D), 131.56 (C A), 131.87 (C B or C), 132.63 (C B or C), 133.02 (C D), 134.52 (C D), 134.56 (C B or C), 135.10 (C A), 137.57 (C D), 137.73 (C A), 137.84 (C B or C), 139.58 (C A), 139.79 (C B or C), 140.55 (C B or C), 140.81 (C D), 211.45 (C=O A), 211.77 (C=O D). IR (neat): 1709 cm<sup>-1</sup> (C=O). MS: M<sup>+</sup> = 382.1799 (calc. for C<sub>23</sub>H<sub>30</sub>OSSi = 382.1787).

**Phenylthio(3-methyl)benzyl lithium (7) and 5-Trimethylsilyl-2-cyclohexen-1-one (8): THF Dependence in Et<sub>2</sub>O at -120 °C.** The general procedure was used with the following changes: 49.0 μL (53.6 mg, 0.25 mmol) of 7-H and 46.6 μL (42.0 mg, 0.25 mmol) of 8 were used; 3 mL of Et<sub>2</sub>O was used as the solvent for 6-H; 1 mL of Et<sub>2</sub>O was used as the solvent for 8; and THF was used in place of HMPA (5 equiv. = 0.10 mL). The metalation was performed at 0 °C for 10 minutes before cooling to -120 °C.

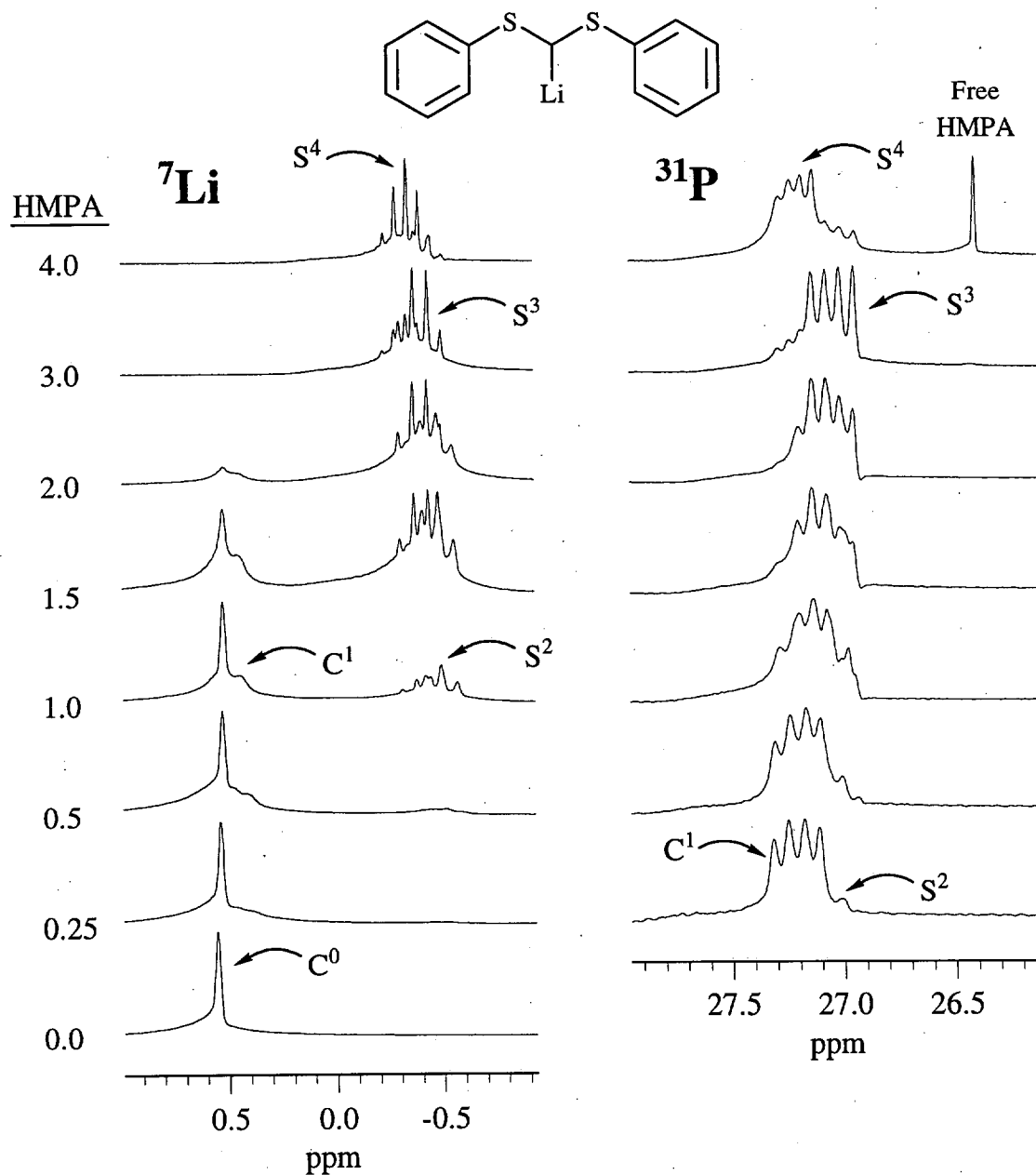
## NMR Spectroscopy

For the characterization of synthesized compounds,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired on a Bruker AC-300 spectrometer with  $\text{CDCl}_3$  as the solvent (unless otherwise stated) and tetramethylsilane as the internal standard.

All multinuclear NMR experiments were performed in 10 mm NMR tubes using a wide-bore AM-360 spectrometer at 139.962 MHz ( $^7\text{Li}$ ). The digital resolution was 0.51 Hz. For a typical 0.15 M solution, excellent signal to noise ratios were obtained after 32 transients.

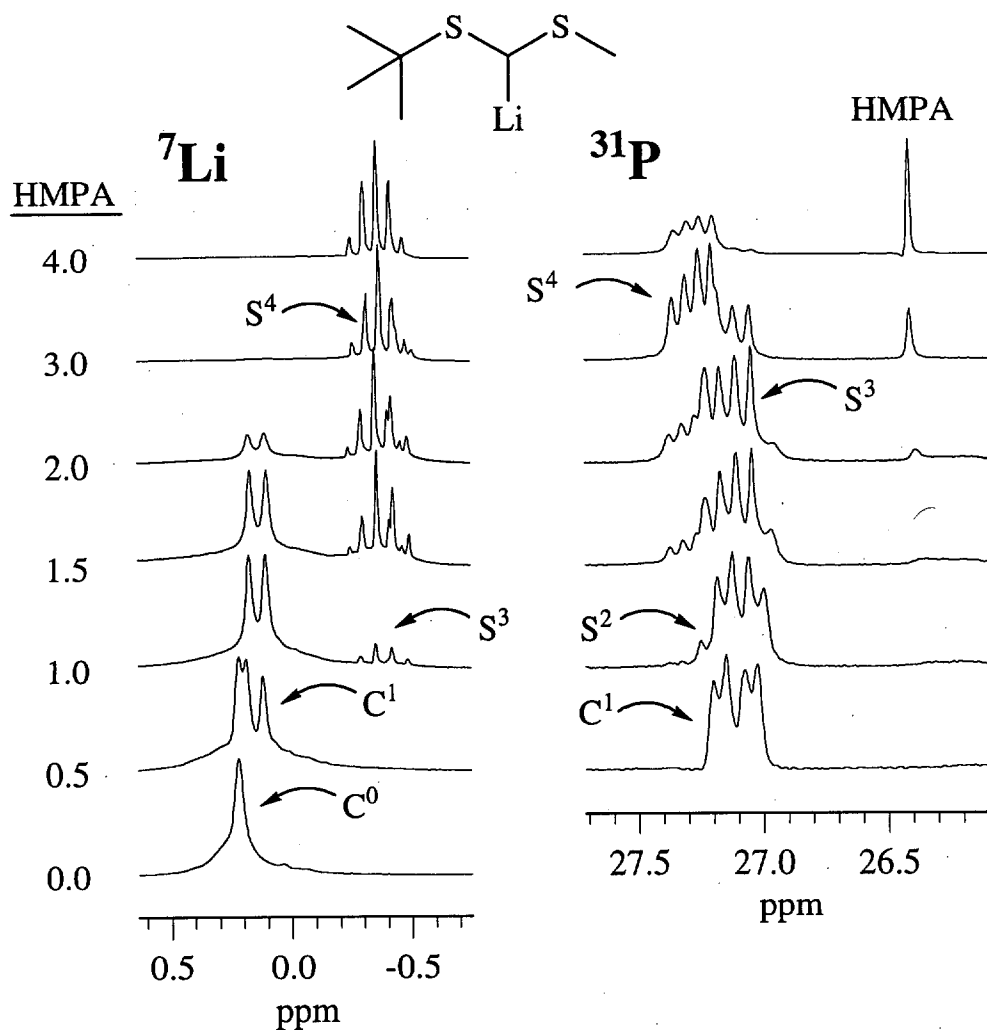
The lithium reagent samples were prepared in 10 mm thin-walled NMR tubes which were oven-dried, fitted with a septum (9 mm i.d.), and  $\text{N}_2$ -flushed. The outside top portion of the tube was lightly greased to make a better seal for the septum, which was held securely in place with parafilm. Silicon grease was placed on the septum top to seal punctures, and the tubes were stored at  $-78\text{ }^\circ\text{C}$  until the experiment was performed. Since non-deuterated solvents were used, the spectrometer was run unlocked, and shimming was performed on the  $^{13}\text{C}$  FID of carbon 3 of THF. Although the spectrometer was unlocked during the acquisition, the field was generally very stable and only occasionally did a spectrum have to be retaken due to a field shift. When HMPA had to be added, the sample was ejected and placed in a  $-78\text{ }^\circ\text{C}$  bath. In order to get HMPA to dissolve, the tube had to be repeatedly shaken, but each time was returned quickly to the cold bath. Temperatures were measured using a thermocouple submerged in a second NMR tube containing the same solvent mixture. In the Figures below, the symbols  $\text{C}^0$ ,  $\text{C}^1$ ,  $\text{C}^2$  refer to the signals for contact ion pairs with 0, 1, or 2 coordinated HMPA molecules on lithium.  $\text{S}^0$ ,  $\text{S}^1$ , etc refer to separated ion pairs with the appropriate number of coordinated HMPA molecules.

**Bis(Phenylthio)methylithium (3).** To a dried, N<sub>2</sub>-purged, 10 mm NMR tube fitted with a septum and maintained under positive N<sub>2</sub> pressure were added 116 mg (0.500 mmol) of *bis*(phenylthio)methane (3-H), 1.8 mL of THF, and 1.2 mL of Et<sub>2</sub>O. The NMR tube was cooled to -78 °C and 0.25 mL (0.500 mmol) of 2.0 M *n*-BuLi in pentane was added. A series of <sup>7</sup>Li spectra at -125 °C were taken during an HMPA titration (1 equiv. of HMPA = 87.0 μL). The spectra are shown in Fig. S1.



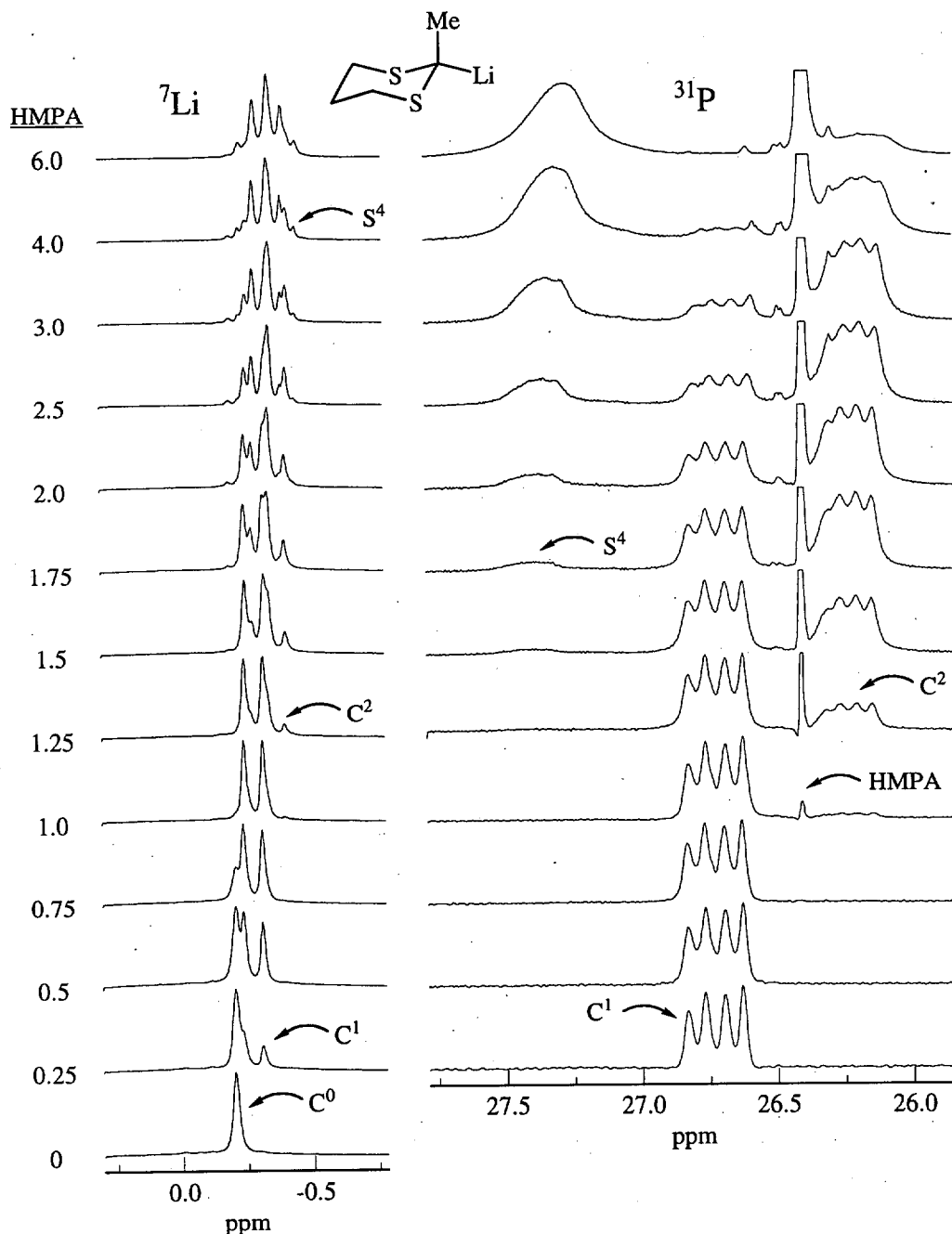
**Figure S1:** <sup>7</sup>Li and <sup>31</sup>P NMR spectra for an HMPA titration of 0.16 M *bis*(phenylthio)methylithium (3) in 3:2 THF/Et<sub>2</sub>O at -125 °C.

***t*-Butylthio(methylthio)methylithium (4).** To a dried, N<sub>2</sub>-purged, 10 mm NMR tube fitted with a septum and maintained under positive N<sub>2</sub> pressure were added 78.4 μL (75.1 mg, 0.500 mmol) of *t*-butylthio(methylthio)methane (4-H), 1.8 mL of THF, and 1.2 mL of Et<sub>2</sub>O. The NMR tube was cooled to -78 °C and 0.32 mL (0.506 mmol) of 1.58 M *t*-BuLi in pentane was added. The NMR tube was warmed to -20 °C until the characteristic bright yellow color of *t*-BuLi in THF had dissipated (approximately 5 min.). A series of <sup>7</sup>Li spectra at -119 °C were taken during an HMPA titration (1 equiv. of HMPA = 87.0 μL). The spectra are shown in Fig. S2.



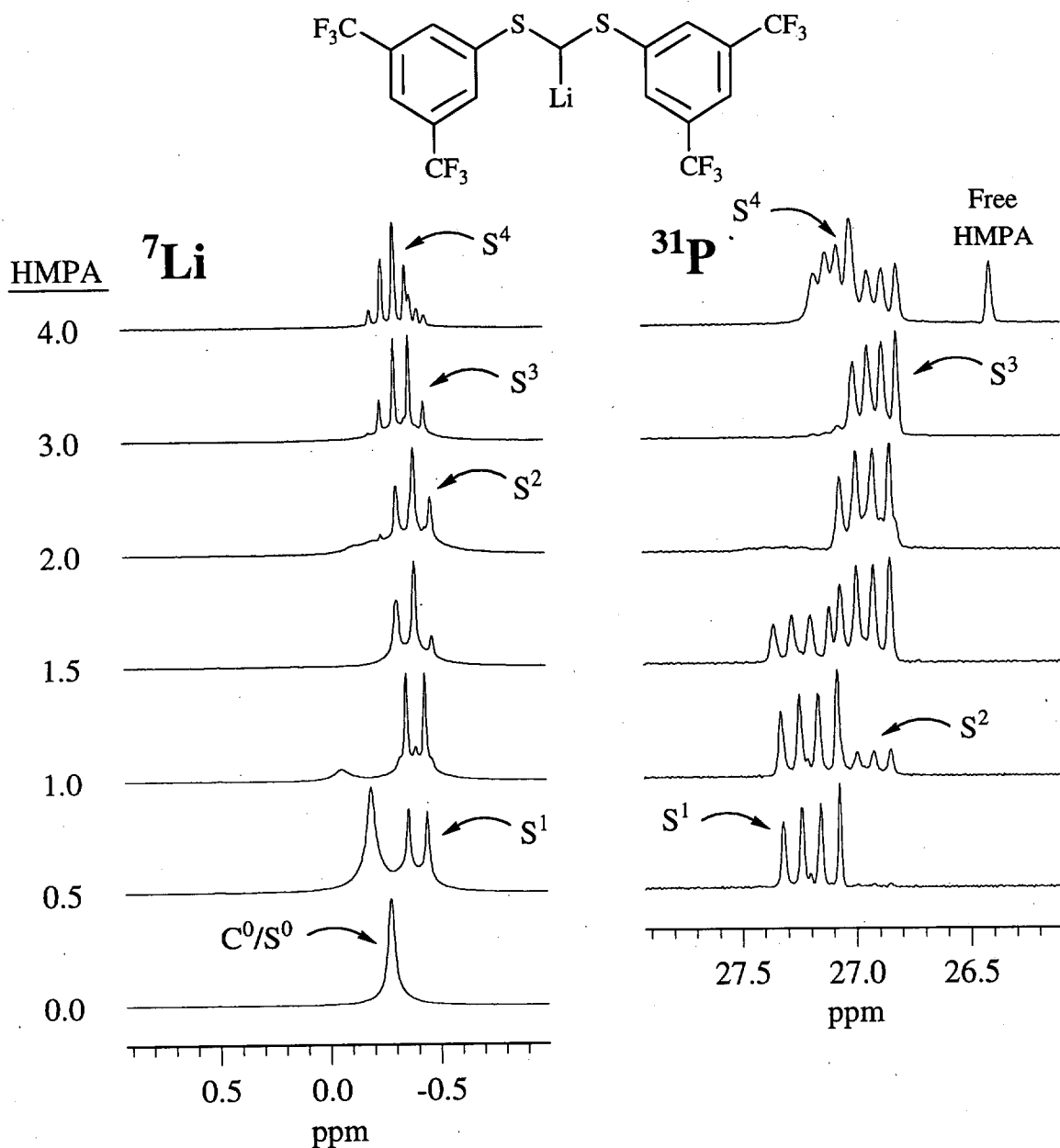
**Figure S2:** <sup>7</sup>Li and <sup>31</sup>P NMR spectra from an HMPA titration of 0.16 M *t*-butylthio(methylthio)methylithium (4) in 3:2 THF/Et<sub>2</sub>O at -119 °C.

**2-Methyl-1,3-dithianyllithium (5).** To a dried, N<sub>2</sub>-purged, 10 mm NMR tube fitted with a septum and maintained under positive N<sub>2</sub> pressure were added 72.5 mg (0.540 mmol) of 2-methyl-1,3-dithiane (5-H), 2.1 mL of THF, and 1.4 mL of Et<sub>2</sub>O. The NMR tube was cooled to -78 °C and 0.25 mL (0.540 mmol) of 2.13 M *n*-BuLi in pentane was added. The NMR tube was warmed to -20 °C for 5 hours to complete the metallation. A series of <sup>7</sup>Li NMR spectra at -135 °C were taken during an HMPA titration (1 equiv. of HMPA = 93.8 μL). The spectra are shown in Fig. S3.



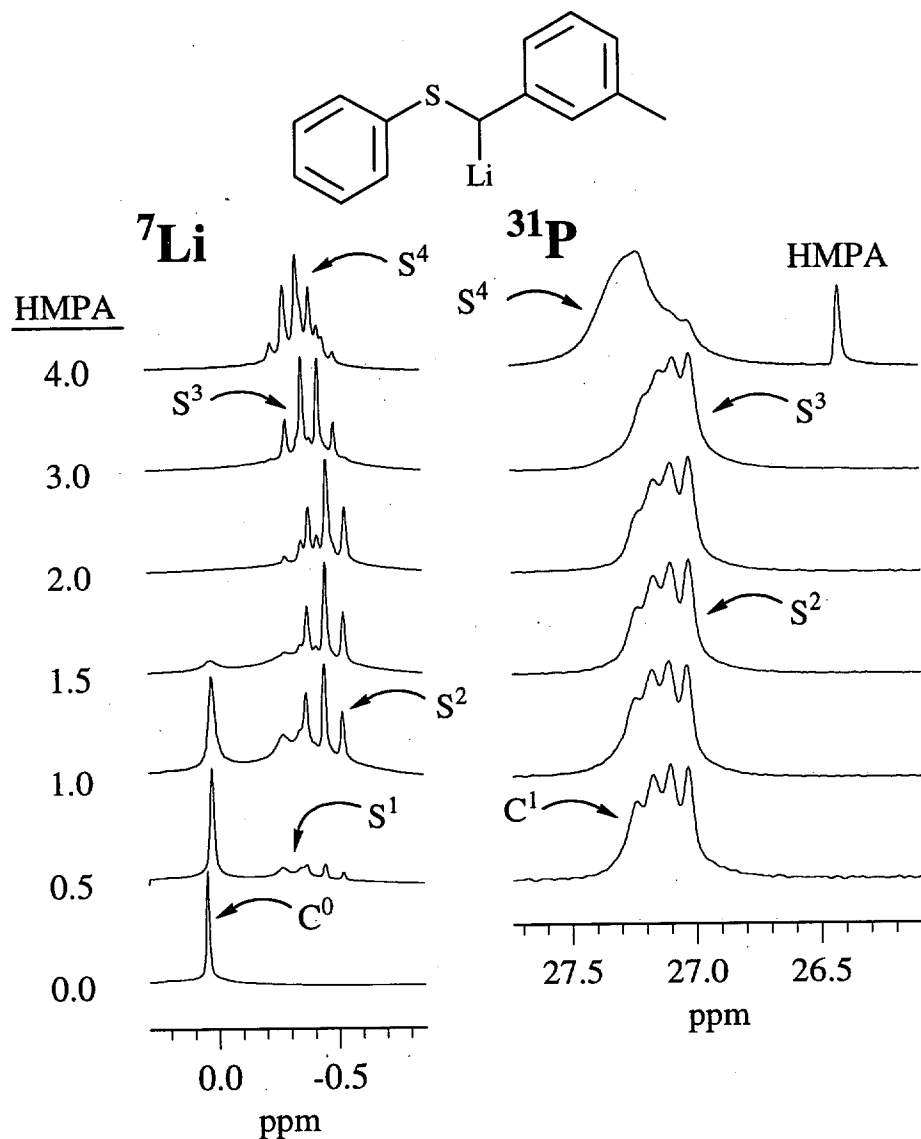
**Figure S3:** <sup>7</sup>Li and <sup>31</sup>P NMR spectra from an HMPA titration of 0.16 M 2-methyl-1,3-dithianyllithium (5) in 3:2 THF/Et<sub>2</sub>O at -135 °C.

**Bis[3,5-Bis(Trifluoromethyl)phenylthio]methylithium (6).** To a dried, N<sub>2</sub>-purged, 10 mm NMR tube fitted with a septum and maintained under positive N<sub>2</sub> pressure were added 154 mg (0.305 mmol) of 3,3',5,5'-*tetrakis*(trifluoromethyl)*bis*(phenylthio)methane (6-H), 1.8 mL of THF, and 1.2 mL of Et<sub>2</sub>O. The NMR tube was cooled to -78 °C and 0.14 mL (0.298 mmol) of 2.13 M *n*-BuLi in pentane was added. A series of <sup>7</sup>Li spectra at -130 °C were taken during an HMPA titration (1 equiv. of HMPA = 51.9 μL). The spectra are shown in Fig. S4.



**Figure S4:** <sup>7</sup>Li and <sup>31</sup>P NMR spectra from an HMPA titration of 0.10 M bis[3,5-*bis*(trifluoromethyl)phenylthio]methylithium (6) in 3:2 THF/Et<sub>2</sub>O at -130 °C.

**Phenylthio(3-methyl)benzylithium (7).** To a dried, N<sub>2</sub>-purged, 10 mm NMR tube fitted with a septum and maintained under positive N<sub>2</sub> pressure were added 103  $\mu$ L (108 mg, 0.504 mmol) of 3-methylbenzyl phenyl sulfide (7-H), 1.8 mL of THF, and 1.2 mL of Et<sub>2</sub>O. The NMR tube was cooled to -78  $^{\circ}$ C and 0.27 mL (0.513 mmol) of 1.9 M *n*-BuLi in pentane was added. A series of <sup>7</sup>Li NMR spectra at -127  $^{\circ}$ C were taken during an HMPA titration (1 equiv. of HMPA = 87.7  $\mu$ L). The spectra are shown in Fig. S4.



**Figure S5:** <sup>7</sup>Li and <sup>31</sup>P NMR spectra from an HMPA titration of 0.16 M phenylthio(3-methyl)benzylithium (7) in 3:2 THF/Et<sub>2</sub>O at -129  $^{\circ}$ C.

### Supplementary References

- [1] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165-8.
- [2] Abel, E. W.; Orrell, K. G.; Rahoo, H.; Šik, V. *J. Organomet. Chem.* **1992**, *441*, 255-63.
- [3] Asaoka, M.; Shima, K.; Takei, H. *Tetrahedron Lett.* **1987**, *28*, 5669-72.
- [4] Moore, E. J.; Waymouth, R. *C&EN* **1997**, *75*, 6. Urben, P. G. *C&EN* **1996**, *74*, 3.  
Bretherick, L. *Chem. and Ind.* **1971**, 1017. Appleby, I. C. *Chem. and Ind.* **1971**, 120.
- [5] Ager, D. J.; East, M. B. *J. Org. Chem.* **1986**, *51*, 3983-92.