

### **I. Purification of TMEDA.**

A 3 L round bottom flask fitted with a stir bar was charged with 1.5 L of reagent grade MeOH and 500 mL of TMEDA. The reaction was cooled in an ice bath and 550 mL of concentrated HCl was added slowly over 1.5 hr. An additional 600 mL of MeOH were added, and the mixture was placed in a -40 °C freezer overnight. The solid was collected on a Buchner funnel and then resuspended in 1500 mL of refluxing MeOH. Water (450 mL) was added step-wise until the solution became homogeneous. The mixture was allowed to cool to room temperature for two hours and was then placed in a -40 °C freezer overnight. The solid was collected again on a Buchner funnel and recrystallized once more from 1.5 L of MeOH and 350 mL of water. The white crystalline solid was collected on a Buchner funnel and dried under a full vacuum for three hours. The free base of TMEDA was regenerated by adding 500 g of solid KOH to the hydrochloride salt. After sufficient mixing, the liquid was decanted off and dried over fresh KOH. The solution was again decanted and further dried sequentially with solid CaH<sub>2</sub> and KH in mineral oil. The liquid was vacuum transferred onto sodium and benzophenone. The resulting purple solution was vacuum transferred onto and stored over sodium-lead alloy. TMEDA was freshly vacuum transferred immediately prior to use.

## II. Determination of the Pseudo-First-Order Rate Constants ( $k_{\text{obsd}}$ ).

Each rate constant was determined by quenching ten separate reaction vials as a function of time as described for the following representative procedure: Ten oven-dried, nitrogen-flushed 5 mL serum vials (Kimble) fitted with rubber septa and stir bars were charged sequentially with TMEDA (302  $\mu\text{L}$ , 2.0 mmol), pentane (553  $\mu\text{L}$ ), and *n*-BuLi (125  $\mu\text{L}$ , 0.30 mmol, 2.40 M) at 0 °C. A stock solution of substrate was prepared by dissolving the arene (1.00 mmol) and decane (125  $\mu\text{L}$ , 0.55 mmol) in 2.0 mL of pentane under nitrogen. A second stock solution was prepared by dissolving TMSCl (3.81 mL, 30 mmol) and  $\text{NEt}_3$  (4.18 mL, 30 mmol) in 50 mL of pentane. ( $\text{NEt}_3$  precipitates the residual HCl.) The reactions were initiated by adding aliquots of the arene/pentane solution (20  $\mu\text{l}$ , 0.01 mmol of arene) to each vial. The reactions were quenched at varying times (3-120 minutes) by adding aliquots of the TMSCl/ $\text{NEt}_3$  solution (1 mL, 0.60 mmol of TMSCl) and allowing the reactions to warm to room temperature for 30 minutes. Water (2 mL) was added to each vial and, after complete mixing, the organic layer was removed for direct GC analysis. Control experiments showed no significant partitioning of the arene, the orthosilylated arene, and decane.

Gas chromatography was performed on a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a Hewlett Packard 6890 Series Autosampler Controller and a Hewlett Packard 3396 Series III Integrator. The data were analyzed using the Scientist<sup>TM</sup> software package from MicroMath<sup>®</sup> Scientific Software, Salt Lake City, Utah. All starting material and product intensities were normalized using the decane internal standard prior to least squares analysis.

The disappearance of arene ("A") was fit to the expression

$$[A]/[A_0] = e^{-k_{\text{obsd}}t} \quad (1)$$

where [A] is the concentration of arene (relative to the internal decane standard) at time "t" and [A<sub>0</sub>] is the concentration of arene at t = 0. The appearance of the silylated arene ("P") was fitted to the expression

$$[P] = [P_{\infty}](1 - e^{-k_{\text{obsd}}t}) \quad (2)$$

where [P] is the measured concentration of product at time "t", [P<sub>∞</sub>] is the concentration of product at t = ∞. The measured values of  $k_{\text{obsd}}$  were equal to those determined according to eq 1 ( $\pm 10\%$ ).

We evaluated a third equation for determining the pseudo-first-order rate constant of the form:

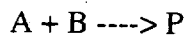
$$[A]/[A_0] = e^{-k_{\text{obsd}}t} + b \quad (3)$$

where "b" is a measure of the amount of arene remaining at t = ∞. The rate constants were not significantly different and the values of b were typically a positive number equal to about 5% of [A<sub>0</sub>]. We report rate constants derived solely from equation 1 for the paper.

Determination of the kinetic isotope effect: The procedure described above was employed using perdeuterated substrates. The reported values of  $k_{\text{H}}/k_{\text{D}}$  are the result of averaged runs (Table 1).

### III. Determination of Orders by the Method of Initial Rates.

Given the reaction



then

$$d[P]/dt = k[A]^a[B]^b$$

At early (low) conversion...

$$d[P]/dt \approx \Delta[P]/\Delta t = k[A]^a[B]^b$$

Let...

abs = absorbance of P measured over time (t) relative to a fixed GC standard

abs<sub>k</sub> = absorbance of a known concentration of product, [P<sub>k</sub>]

Then...

$$[P] = (\text{abs})([P_k]/\text{abs}_k)$$

and...

$$\Delta[P]/\Delta t = (\Delta\text{abs}/\Delta t)([P_k]/\text{abs}_k)$$

Therefore, the rate constant can be obtained by the expression...

$$\Delta\text{abs}/\Delta t = k[A]^a[B]^b(\text{abs}_k/[P_k])$$

Note: The slope, ( $\Delta[P]/\Delta t$ ), will be linearly dependent on [A] if, and only if, the reaction is first order in 'A'. This is true whether 'A' is the substrate (benzene), organolithium (*n*-BuLi/TMEDA), or ligand (TMEDA). Also,  $\Delta[P]/\Delta t$  will be directly proportional to the reaction rate constant.

The initial rates of product formation were determined by least squares analyses using the equation

$$[P] = (\Delta[P]/\Delta t)*t + C \quad (\text{e.g., } y = mx + b) \quad (4)$$

where C is the deviation for an ideal intercept value of zero. The typically small, but positive C term is attributed to an unavoidable slight warming of the initial reaction at time zero when the final reagent (*n*-BuLi) is added.

IV. Tables of relative rate data. All reactions were run with *n*-BuLi (1.0 M), TMEDA (1.5 M), and aromatic substrate (0.01 M) in pentane cosolvent at 0 °C.

Product ratios for the formation of C<sub>6</sub>H<sub>5</sub>-TMS relative to C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-2-TMS at early conversion.

Ratio	Ratio (avg)
0.00102	0.0012 ± 1E-4
0.00127	
0.00128	
0.00121	
0.00125	
0.00128	

$k_{\text{obsd}}$  (s<sup>-1</sup>) for the metalation of *m*-C<sub>6</sub>H<sub>4</sub>(OCH<sub>3</sub>)<sub>2</sub> relative to C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>.

<i>m</i> -C <sub>6</sub> H <sub>4</sub> (OCH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	Ratio (avg)
0.057 ± 7E-3	0.00094 ± 3E-5	57 ± 6
0.047 ± 4E-3	0.00090 ± 1E-5	

$k_{\text{obsd}}$  (s<sup>-1</sup>) for the metalation of C<sub>6</sub>H<sub>5</sub>OCH<sub>2</sub>OCH<sub>3</sub> relative to C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>.

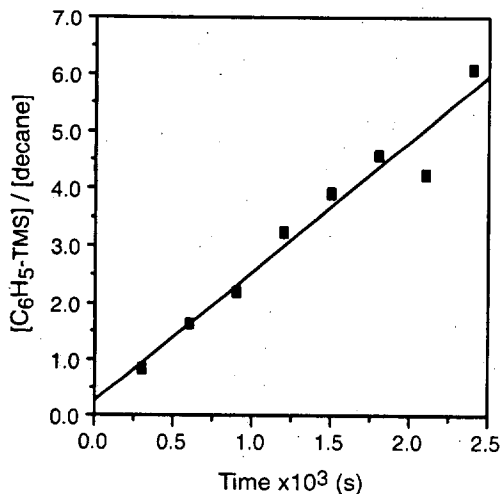
C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> OCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	Ratio (avg)
0.013 ± 1E-3	0.00087 ± 6E-5	14 ± 1
0.013 ± 1E-3	0.0010 ± 1E-4	

$k_{\text{obsd}}$  (s<sup>-1</sup>) for the metalation of C<sub>6</sub>H<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> relative to C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>.

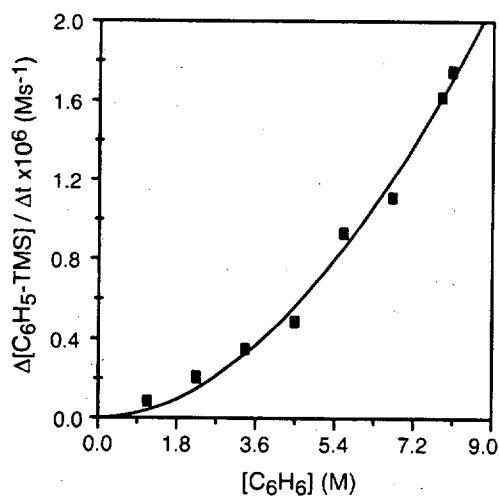
C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	Ratio (avg)
0.0024 ± 2E-4	0.00091 ± 2E-5	2.5 ± 0.1
0.0022 ± 2E-4	0.00090 ± 1E-5	

$k_{\text{obsd}}$  (s<sup>-1</sup>) for the metalation of C<sub>6</sub>H<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> relative to C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>.

C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	Ratio (avg)
0.0012 ± 1E-4	0.00091 ± 2E-5	1.3 ± 0.1
0.0012 ± 1E-4	0.00090 ± 1E-5	

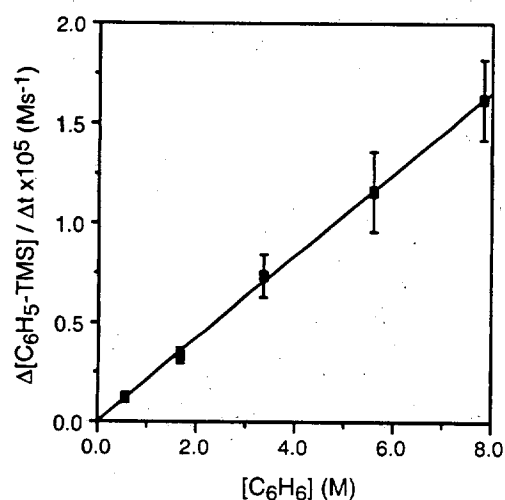


V. Representative plot of  $[\text{C}_6\text{H}_5\text{-TMS}]/[\text{decane}]$  vs. time for the metalation of  $\text{C}_6\text{H}_6$  (7.8 M) by  $n\text{-BuLi}$  (0.3 M) in TMEDA (1.3 M) and pentane cosolvent at  $0^\circ\text{C}$ . The curve depicts the result of an unweighted least-squares fit to  $[\text{C}_6\text{H}_5\text{-TMS}]/[\text{decane}] = (\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t)t + [\text{C}_6\text{H}_5\text{-TMS}]_0$ ;  $(\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t = (1.6 \pm 0.1) \times 10^{-5}$ ,  $[\text{C}_6\text{H}_5\text{-TMS}]_0 = 0.3 \pm 0.3$ ).



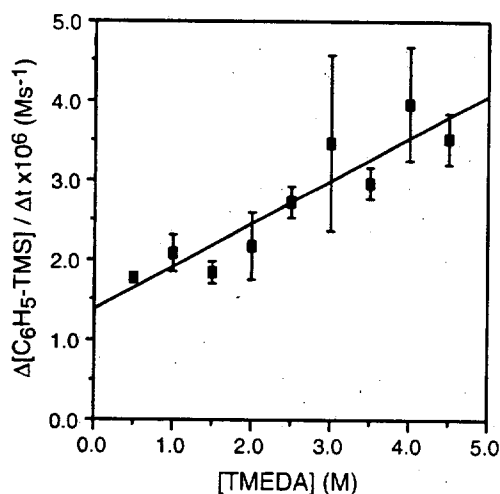
[C <sub>6</sub> H <sub>6</sub> ] (M)	Δ[C <sub>6</sub> H <sub>5</sub> -TMS]/Δt (Ms <sup>-1</sup> )
1.1	0.00000088 ± 1E-8
2.2	0.0000021 ± 2E-7
3.4	0.0000035 ± 2E-7
4.5	0.0000049 ± 4E-7
5.6	0.000009 ± 2E-6
6.7	0.000011 ± 7E-6
7.8	0.000016 ± 2E-6
8.1	0.000018 ± 1E-6

VI. Plot of  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t$  vs.  $[\text{C}_6\text{H}_6]$  for metalation by  $n\text{-BuLi}$  (0.3 M) in TMEDA (1.3 M) and pentane cosolvent at  $0^\circ\text{C}$ . The curve depicts the result of an unweighted least-squares fit to  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t = k[\text{C}_6\text{H}_6]^n$ ;  $(k = (0.2 \pm 0.1) \times 10^{-7}$ ,  $n = 1.9 \pm 0.1$ ).



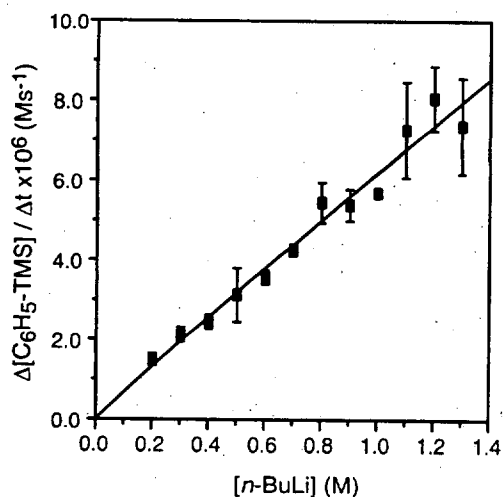
[C <sub>6</sub> H <sub>6</sub> ] (M)	Δ[C <sub>6</sub> H <sub>5</sub> -TMS]/Δt (avg) (Ms <sup>-1</sup> )
0.6	0.00000123 ± 19E-8
1.7	0.00000331 ± 39E-8
3.4	0.00000733 ± 11E-8
5.6	0.0000116 ± 20E-7
7.8	0.0000162 ± 20E-7

**VII.** Plot of  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t$  vs.  $[\text{C}_6\text{H}_6]$  for metalation by *n*-BuLi (0.3 M) in TMEDA (1.3 M) in  $\text{C}_6\text{D}_6$  and pentane cosolvents at 0 °C. Total  $[\text{C}_6\text{H}_6 + \text{C}_6\text{D}_6]$  is fixed at 7.8 M. The curve depicts the result of an unweighted least-squares fit to  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t = k[\text{C}_6\text{H}_6]^n$ ; ( $k = (1.9 \pm 0.3) \times 10^{-6}$ ,  $n = 0.98 \pm 0.03$ ).



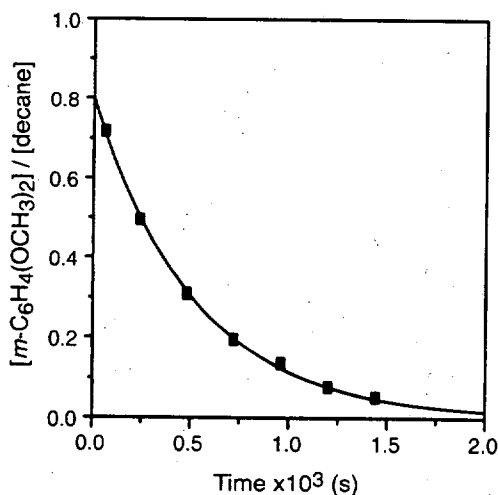
[TMEDA] (M)	Δ[C <sub>6</sub> H <sub>5</sub> -TMS]/Δt (avg) (Ms <sup>-1</sup> )
0.5	0.00000177 ± 4E-8
1.0	0.00000208 ± 23E-8
1.5	0.00000184 ± 14E-8
2.0	0.00000217 ± 42E-8
2.5	0.00000272 ± 20E-8
3.0	0.00000346 ± 1E-7
3.5	0.00000296 ± 20E-8
4.0	0.00000396 ± 71E-8
4.5	0.00000352 ± 32E-8

**VIII.** Plot of  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t$  vs. free [TMEDA] for the metalation of  $\text{C}_6\text{H}_6$  (2.2 M) by *n*-BuLi (0.3 M) in pentane cosolvent at 0 °C. The curve depicts the result of an unweighted least-squares fit to  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t = k[\text{TMEDA}] + k'$ ; ( $k = (5.9 \pm 0.9) \times 10^{-7}$ ,  $k' = (1.4 \pm 0.3) \times 10^{-6}$ ).

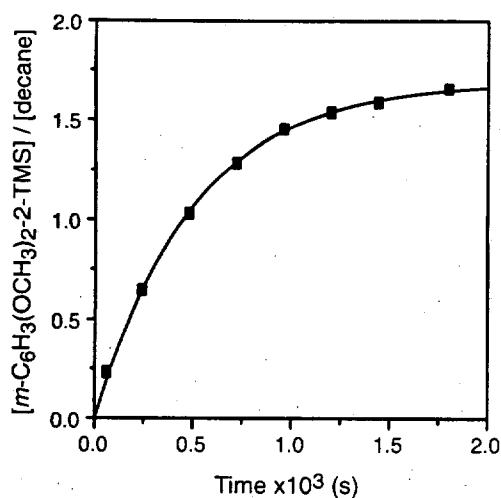


[ <i>n</i> -BuLi] (M)	Δ[C <sub>6</sub> H <sub>5</sub> -TMS]/Δt (avg) (Ms <sup>-1</sup> )
0.2	0.00000150 ± 15E-8
0.3	0.00000213 ± 19E-8
0.4	0.00000246 ± 18E-8
0.5	0.00000313 ± 67E-8
0.6	0.00000357 ± 18E-8
0.7	0.00000427 ± 16E-8
0.8	0.00000545 ± 50E-8
0.9	0.00000539 ± 39E-8
1.0	0.00000569 ± 9E-8
1.1	0.00000728 ± 12E-7
1.2	0.00000807 ± 81E-8
1.3	0.00000738 ± 12E-7

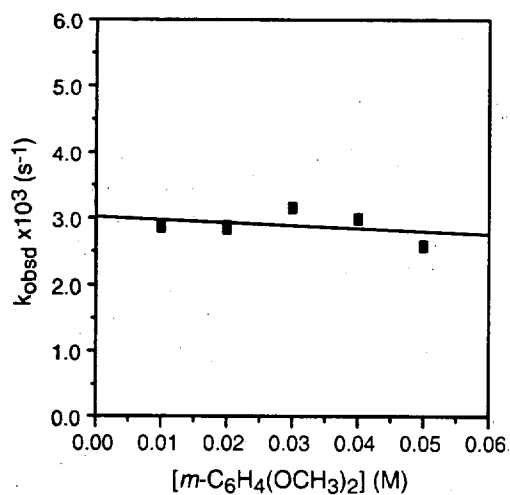
IX. Plot of  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t$  vs.  $[\textit{n}\text{-BuLi}]$  for the metalation of  $\text{C}_6\text{H}_6$  (2.2 M) in TMEDA (1.0 M excess relative to base) and pentane cosolvent at 0 °C. The curve depicts the result of an unweighted least-squares fit to  $\Delta[\text{C}_6\text{H}_5\text{-TMS}]/\Delta t = k[\textit{n}\text{-BuLi}]^n$ ; ( $k = (6.2 \pm 0.2) \times 10^{-6}$ ,  $n = 0.96 \pm 0.07$ ).



X. Representative plot of  $[m\text{-C}_6\text{H}_4(\text{OCH}_3)_2]/[\text{decane}]$  vs. time for the metalation of  $m\text{-C}_6\text{H}_4(\text{OCH}_3)_2$  (0.01 M) by  $\textit{n}\text{-BuLi}$  (0.7 M) in TMEDA (1.2 M) and pentane cosolvent at -35 °C. The curve depicts the result of an unweighted least-squares fit to  $[m\text{-C}_6\text{H}_4(\text{OCH}_3)_2]/[\text{decane}] = [m\text{-C}_6\text{H}_4(\text{OCH}_3)_2]_0 e^{-k_{\text{obsd}}t}$ ; ( $[m\text{-C}_6\text{H}_4(\text{OCH}_3)_2]_0 = 0.80 \pm 0.01$ ,  $k_{\text{obsd}} = (1.94 \pm 0.04) \times 10^{-3}$ ).



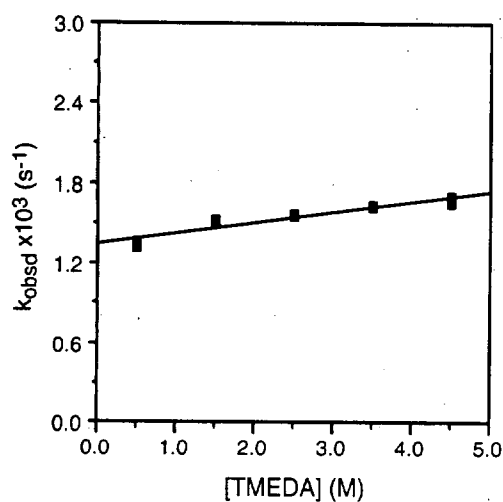
**XI.** Representative plot of  $[m\text{-C}_6\text{H}_3(\text{OCH}_3)_2\text{-2-TMS}]/[\text{decane}]$  vs. time for the metalation of  $m\text{-C}_6\text{H}_4(\text{OCH}_3)_2$  (0.01 M) by  $n\text{-BuLi}$  (0.7 M) in TMEDA (1.2 M) and pentane cosolvent at  $-35^\circ\text{C}$ . The curve depicts the result of an unweighted least-squares fit to  $[m\text{-C}_6\text{H}_4(\text{OCH}_3)_2\text{-2-TMS}]/[\text{decane}] = [m\text{-C}_6\text{H}_4(\text{OCH}_3)_2\text{-2-TMS}]_\infty(1 - e^{-k_{\text{obsd}}t})$ ;  $([m\text{-C}_6\text{H}_4(\text{OCH}_3)_2\text{-2-TMS}]_\infty = 1.70 \pm 0.02, k_{\text{obsd}} = (1.99 \pm 0.06) \times 10^{-3})$ .



$[m\text{-C}_6\text{H}_4(\text{OCH}_3)_2]$ (M)	$k_{\text{obsd}}$ (avg) ( $\text{s}^{-1}$ )
0.01	$0.00287 \pm 5\text{E-}5$
0.02	$0.00286 \pm 9\text{E-}5$
0.03	$0.00316 \pm 5\text{E-}5$
0.04	$0.00299 \pm 4\text{E-}5$
0.05	$0.00258 \pm 7\text{E-}5$

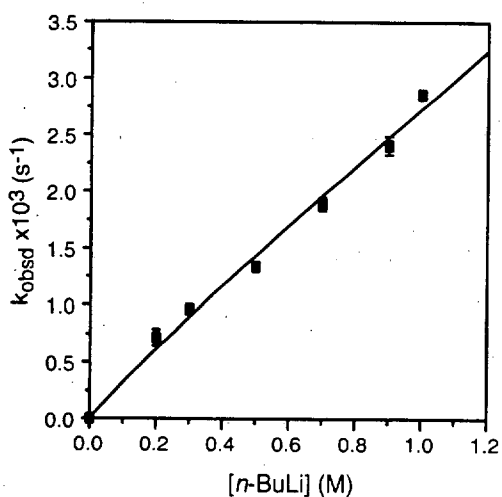
**XII.** Plot of  $k_{\text{obsd}}$  vs.  $[m\text{-C}_6\text{H}_4(\text{OCH}_3)_2]$  for metalation by  $n\text{-BuLi}$  (1.0 M) in TMEDA (1.5 M) and pentane cosolvent at  $-35^\circ\text{C}$ . The curve depicts the result of an unweighted least-squares fit to  $k_{\text{obsd}} = k[m\text{-C}_6\text{H}_4(\text{OCH}_3)_2] + k'$ ;  $(k = -(4.0 \pm 7.0) \times 10^{-3}, k' = 3.0 \pm 0.2 \times 10^{-3})$ .





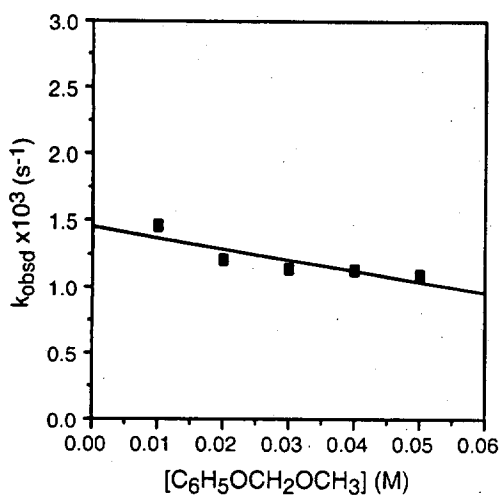
[TMEDA] (M)	$k_{\text{obsd}} \text{ (avg) (s}^{-1}\text{)}$
0.5	$0.00134 \pm 5\text{E-}5$
1.5	$0.00152 \pm 4\text{E-}5$
2.5	$0.00156 \pm 3\text{E-}5$
3.5	$0.00163 \pm 3\text{E-}5$
4.5	$0.00168 \pm 6\text{E-}5$

**XIII.** Plot of  $k_{\text{obsd}}$  vs. free [TMEDA] for the metalation of  $m\text{-C}_6\text{H}_4(\text{OCH}_3)_2$  (0.01 M) by  $n\text{-BuLi}$  (0.5 M) in pentane cosolvent at  $-35^\circ\text{C}$ . The curve depicts the result of an unweighted least-squares fit to  $k_{\text{obsd}} = k[\text{TMEDA}] + k'$ ; ( $k = (8.0 \pm 1.0) \times 10^{-5}$ ,  $k' = (1.34 \pm 0.04) \times 10^{-3}$ ).



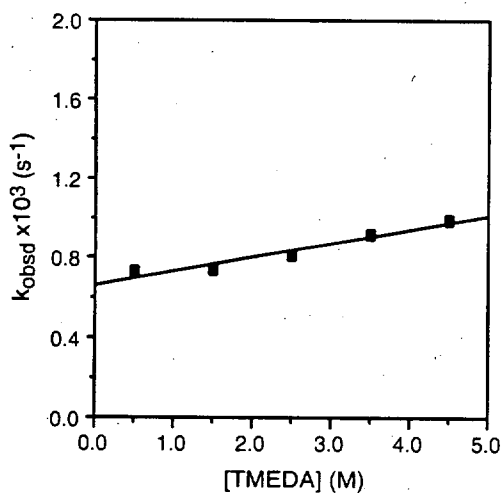
[n-BuLi] (M)	$k_{\text{obsd}} \text{ (avg) (s}^{-1}\text{)}$
0.2	$0.00072 \pm 92\text{E-}6$
0.3	$0.00096 \pm 25\text{E-}6$
0.5	$0.00134 \pm 5\text{E-}5$
0.7	$0.00189 \pm 7\text{E-}5$
0.9	$0.00241 \pm 10\text{E-}5$
1.0	$0.00287 \pm 5\text{E-}5$

**XIV.** Plot of  $k_{\text{obsd}}$  vs. [n-BuLi] for the metalation of  $m\text{-C}_6\text{H}_4(\text{OCH}_3)_2$  (0.01 M) in TMEDA (0.5 M excess relative to base) and pentane cosolvent at  $-35^\circ\text{C}$ . The curve depicts the result of an unweighted least-squares fit to  $k_{\text{obsd}} = k[\text{n-BuLi}]^n$ ; ( $k = (2.74 \pm 0.08) \times 10^{-3}$ ,  $n = 0.93 \pm 0.07$ ).



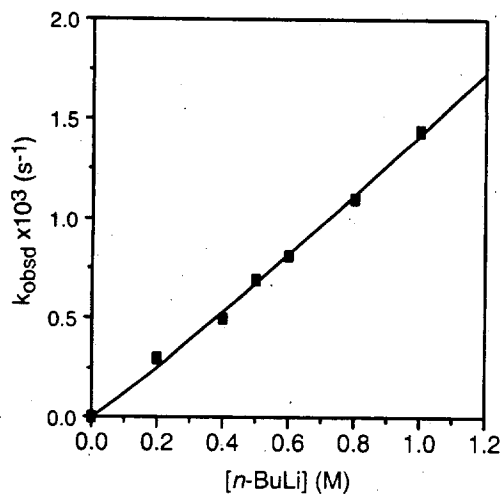
[C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> OCH <sub>3</sub> ] (M)	k <sub>obsd</sub> (s <sup>-1</sup> )
0.01	0.00146 ± 7E-5
0.02	0.00121 ± 3E-5
0.03	0.00114 ± 2E-5
0.04	0.00113 ± 1E-5
0.05	0.00109 ± 3E-5

XV. Plot of  $k_{\text{obsd}}$  vs.  $[\text{C}_6\text{H}_5\text{OCH}_2\text{OCH}_3]$  for metalation by *n*-BuLi (1.0 M) in TMEDA (1.5 M) and pentane cosolvent at -35 °C. The curve depicts the result of an unweighted least-squares fit to  $k_{\text{obsd}} = k[\text{C}_6\text{H}_5\text{OCH}_2\text{OCH}_3] + k'$ ; ( $k = (-8.0 \pm 30) \times 10^{-3}$ ,  $k' = (1.45 \pm 0.09) \times 10^{-3}$ ).



[TMEDA] (M)	k <sub>obsd</sub> (s <sup>-1</sup> )
0.5	0.000727 ± 4E-5
1.5	0.000737 ± 2E-5
2.5	0.000810 ± 1E-5
3.5	0.000919 ± 2E-5
4.5	0.000991 ± 2E-5

XVI. Plot of  $k_{\text{obsd}}$  vs. free [TMEDA] for the metalation of  $\text{C}_6\text{H}_5\text{OCH}_2\text{OCH}_3$  (0.01 M) by *n*-BuLi (0.5 M) in pentane cosolvent at -35 °C. The curve depicts the result of an unweighted least-squares fit to  $k_{\text{obsd}} = k[\text{TMEDA}] + k'$ ; ( $k = 7.0 \pm 1.0 \times 10^{-5}$ ,  $k' = (6.6 \pm 0.3) \times 10^{-4}$ ).



[ <i>n</i> -BuLi] (M)	$k_{\text{obsd}}$ (s <sup>-1</sup> )
0.2	$0.000288 \pm 7\text{E-}6$
0.4	$0.000496 \pm 1\text{E-}5$
0.5	$0.000727 \pm 4\text{E-}5$
0.6	$0.000811 \pm 2\text{E-}5$
0.8	$0.00110 \pm 2\text{E-}5$
1.0	$0.00146 \pm 7\text{E-}5$

**XVII.** Plot of  $k_{\text{obsd}}$  vs. [*n*-BuLi] for the metalation of  $\text{C}_6\text{H}_5\text{OCH}_2\text{OCH}_3$  (0.01 M) in TMEDA (0.5 M excess relative to base) and pentane cosolvent at  $-35^\circ\text{C}$ . The curve depicts the result of an unweighted least-squares fit to  $k_{\text{obsd}} = k[\textit{n}\text{-BuLi}]^n$ ; ( $k = (1.42 \pm 0.03) \times 10^{-3}$ ,  $n = 1.07 \pm 0.04$ ).

**XVIII.** Calculated energies of reactants and transition structures for arene lithiation using Gaussian 98 at the B3LYP level of density functional theory with the 6-31G\* basis set.

	$E_{elec}$ (Hartrees)	H(298.15) <sup>a</sup> (Hartrees)	$\Delta H^\ddagger$ (kcal/mol)
1; C <sub>6</sub> H <sub>6</sub>	-232.24866	-232.14448	---
2; C <sub>6</sub> H <sub>5</sub> OMe	-346.77132	-346.63240	---
<i>syn,anti-3</i> ; <i>syn,anti-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe) <sub>2</sub>	-461.29444	-461.12075	---
<i>syn,syn-3</i> ; <i>syn,syn-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe) <sub>2</sub>	-461.29348	-461.11984	---
<i>anti,anti-3</i> ; <i>anti,anti-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe) <sub>2</sub>	-461.29370	-461.12003	---
15; [(CH <sub>3</sub> ) <sub>2</sub> Li] <sup>-</sup>	-87.32195	-87.25067	---
17; C <sub>6</sub> H <sub>5</sub> F	-331.48230	-331.38534	---
18; <i>m-C</i> <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	-430.71499	-430.62525	---
<i>syn-19</i> ; <i>syn-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe)F	-446.00526	-445.87355	---
<i>anti-19</i> ; <i>anti-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe)F	-446.00497	-445.87331	---
20; C <sub>6</sub> H <sub>5</sub> NMe <sub>2</sub>	-366.21519	-366.03461	---
21; 1,3-benzodioxole	-420.77709	-420.65531	---
22; 2,3-dihydrobenzofuran	-384.88372	-384.73781	---
23; [Me <sub>2</sub> Li·C <sub>6</sub> H <sub>6</sub> ] <sup>-</sup>	-319.54834	-319.37519	12.5
24; [Me <sub>2</sub> Li· <i>syn-C</i> <sub>6</sub> H <sub>5</sub> OMe] <sup>-</sup>	-434.07815	-433.86997	8.2
25; [Me <sub>2</sub> Li· <i>anti-C</i> <sub>6</sub> H <sub>5</sub> OMe] <sup>-</sup>	-434.07727	-433.86989	8.3
26; [Me <sub>2</sub> Li· <i>syn,anti-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe) <sub>2</sub> ] <sup>-</sup>	-548.60608	-548.36361	4.9
27; [Me <sub>2</sub> Li· <i>syn,syn-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe) <sub>2</sub> ] <sup>-</sup>	-548.60102	-548.35798	8.4
28; [Me <sub>2</sub> Li· <i>anti,anti-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe) <sub>2</sub> ] <sup>-</sup>	-548.60010	-548.35810	8.4
29; [Me <sub>2</sub> Li·C <sub>6</sub> H <sub>5</sub> F] <sup>-</sup>	-418.79225	-418.62676	5.8
30; [Me <sub>2</sub> Li· <i>m-C</i> <sub>6</sub> H <sub>4</sub> F <sub>2</sub> ] <sup>-</sup>	-518.03333	-517.87487	0.7
31; [Me <sub>2</sub> Li· <i>syn-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe)F] <sup>-</sup>	-533.32245	-533.12189	1.5
32; [Me <sub>2</sub> Li· <i>anti-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe)F] <sup>-</sup> (Li-F)	-533.31483	-533.11467	6.0
33; [Me <sub>2</sub> Li· <i>anti-m-C</i> <sub>6</sub> H <sub>4</sub> (OMe)F] <sup>-</sup> (Li-OMe)	-533.32002	-533.11973	2.8
34; [Me <sub>2</sub> Li·C <sub>6</sub> H <sub>5</sub> NMe <sub>2</sub> ] <sup>-</sup>	-453.51655	-453.26691	11.5
35; [Me <sub>2</sub> Li·1,3-benzodioxole] <sup>-</sup>	-508.08433	-507.89339	7.9
36; [Me <sub>2</sub> Li·2,3-dihydrobenzofuran] <sup>-</sup>	-472.18570	-471.97079	11.1
46; [MeLi·C <sub>6</sub> H <sub>6</sub> ]	-279.62276	-279.48373	15.3
47; [MeLi· <i>anti-C</i> <sub>6</sub> H <sub>5</sub> OMe]	-394.16497	-393.99133	2.9
48; [MeLi· <i>syn-C</i> <sub>6</sub> H <sub>5</sub> OMe]	-394.14978	-393.97603	12.5
MeLi	-47.40112	-47.36359	---

<sup>a</sup>Enthalpies (H) were calculated at 298,15 K, 1.0 atm and with a scaling factor of 0.9804.