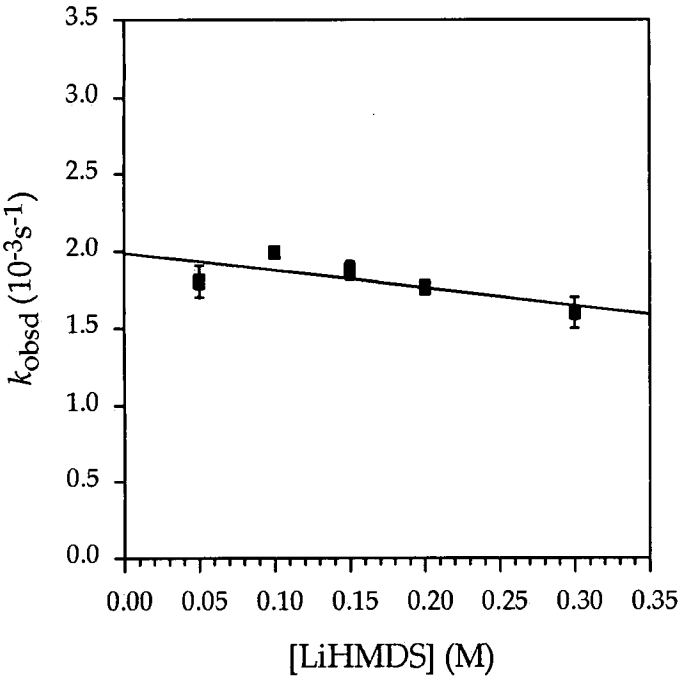
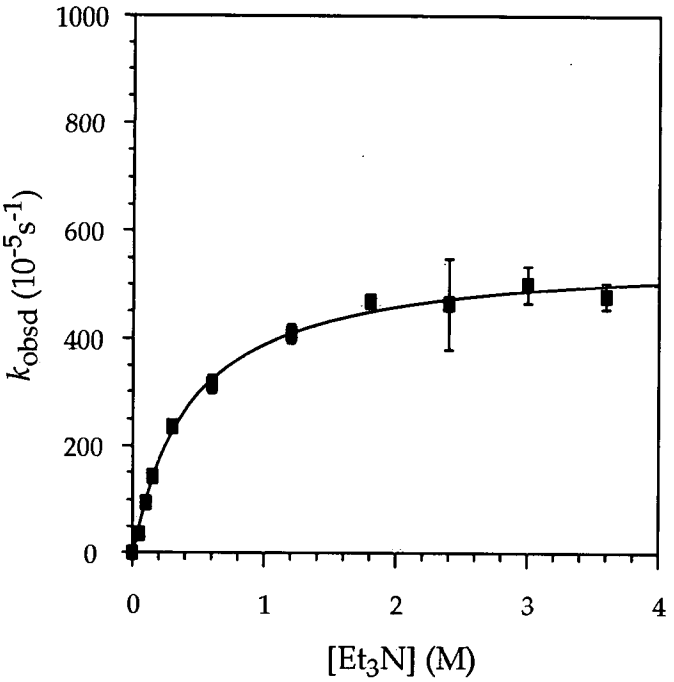



**I.** Plot of $k_{obsd}$ vs [LiHMDS] in toluene for the enolization of **1** (0.004 M) by LiHMDS at –40 °C. The curve depicts the results of an unweighted least-squares fit to $k_{obsd}$ = a[LiHMDS] + b (a = -1.1 ± 0.6 x $10^{-3}$, b = 2.0 ± 0.1 x $10^{-3}$).

**II.** Table of data for plot in section **I.**

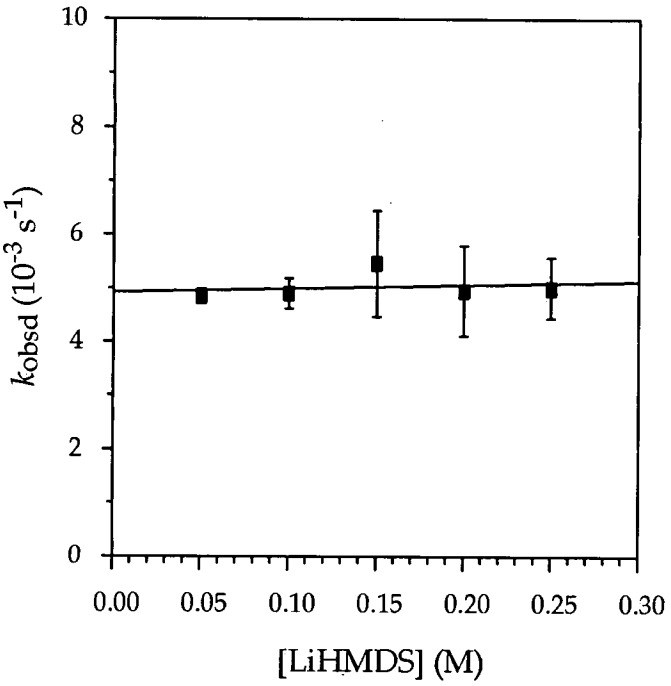
| [LiHMDS] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 1.76 ± 0.03E-3 | 1.95 ± 0.05E-3 | 1.8 ± 0.1E-3 |
| 0.10 | 2.00 ± 0.03E-3 | 1.98 ± 0.02E-3 | 1.99 ± 0.01E-3 |
| 0.15 | 1.81 ± 0.04E-3 | 1.93 ± 0.04E-3 | 1.87 ± 0.06E-3 |
| 0.20 | 1.81 ± 0.04E-3 | 1.72 ± 0.03E-3 | 1.76 ± 0.04E-3 |
| 0.30 | 1.72 ± 0.03E-3 | 1.46 ± 0.03E-3 | 1.6 ± 0.1E-3 |




**III**. Plot of $k_{obsd}$ vs [$Et_3N$] in toluene cosolvent for the enolization of **1-d$_3$** (0.004 M) by LiHMDS (0.10 M) at –78 °C. The curve depicts the results of an unweighted least-squares fit to $k_{obsd}$ = a[$Et_3N$] / (1 + b[$Et_3N$]) (a = 1.25 ± 0.08 x $10^{-2}$, b = 2.2 ± 0.2).

**IV**. Table of data for plot in section **III**.

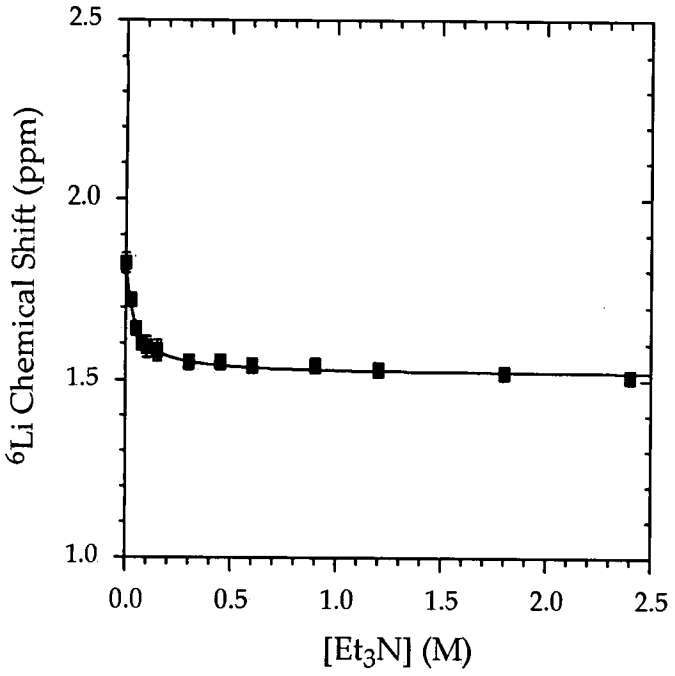
| [$Et_3N$] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 3.8 ± 0.1E-4 | 3.4 ± 0.1E-4 | 3.6 ± 0.3E-4 |
| 0.15 | 1.46 ± 0.02E-3 | 1.40 ± 0.02E-3 | 1.43 ± 0.04E-3 |
| 0.30 | 2.32 ± 0.04E-3 | 2.39 ± 0.03E-3 | 2.36 ± 0.06E-3 |
| 0.60 | 3.02 ± 0.07E-3 | 3.2 ± 0.1E-3 | 3.1 ± 0.1E-3 |
| 1.2 | 4.0 ± 0.2E-3 | 4.2 ± 0.1E-3 | 4.1 ± 0.1E-3 |
| 1.8 | 4.7 ± 0.1E-3 | 4.7 ± 0.2E-3 | 4.7 ± 0.4E-3 |
| 2.4 | 5.0 ± 0.4E-3 | 4.2 ± 0.1E-3 | 4.6 ± 0.8E-3 |
| 3.0 | 4.8 ± 0.2E-3 | 5.3 ± 0.2E-3 | 5.0 ± 0.3E-3 |
| 3.6 | 4.6 ± 0.2E-3 | 5.0 ± 0.1E-3 | 4.8 ± 0.3E-3 |




**V.** Plot of $k_{obsd}$ vs [LiHMDS] for the enolization of **1-d$_3$** (0.004 M) by LiHMDS in 3.0 M $Et_3N$/toluene at –78 °C. The curve depicts the results of an unweighted least-squares fit to $k_{obsd}$ = a[LiHMDS] + b (a = 2 ± 3 x $10^{-3}$, b = 4.8 ± 0.4 x $10^{-4}$).

**VI.** Table of data for plot in section **V**.

| [LiHMDS] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 4.7 ± 0.1E-3 | 4.9 ± 0.2E-3 | 4.8 ± 0.1E-3 |
| 0.10 | 4.8 ± 0.2E-3 | 5.3 ± 0.3E-3 | 5.0 ± 0.3E-3 |
| 0.15 | 5.8 ± 0.4E-3 | 4.4 ± 0.3E-3 | 5 ± 1E-3 |
| 0.20 | 5.3 ± 0.2E-3 | 4.0 ± 0.2E-3 | 4.6 ± 0.8E-3 |
| 0.25 | 5.2 ± 0.7E-3 | 4.4 ± 0.2E-3 | 4.8 ± 0.6E-3 |




**VII**. Plot of $^6$Li chemical shift vs [$Et_3N$] for 0.1 M [$^6$Li,$^{15}$N]LiHMDS in $Et_3N$/pentane mixture at –60 °C. The curve depicts the results of an unweighted least-squares fit to $y = ax/(1 + bx) + c$. The values of the parameters are as follows: $a = -9 \pm 1$ (ppm·M$^{-1}$), $b = K_{eq} = 28 \pm 3$ (M$^{-1}$), $c = 2 \pm 1$.

**VIII**. Enolization rates under non-pseudo-first-order conditions.

| LiHMDS | $10^5 \cdot k_{obsd}$ ($s^{-1}$) | |
|---|---|---|
| equiv | None[a] | $Et_3N$[b] |
| 20 | 200 | 410 |
| 2.0 | 510 | 260 |
| 1.0 | 340 | 5 |

[a]Enolizations of **1** (**1**-$d_0$) were carried out using 0.1 M LiHMDS in toluene at -40 °C.
[b]Enolizations of **1**-$d_3$ were carried out using 0.1 M LiHMDS in toluene at -40 °C.
Comparisons across the rows are not valid.