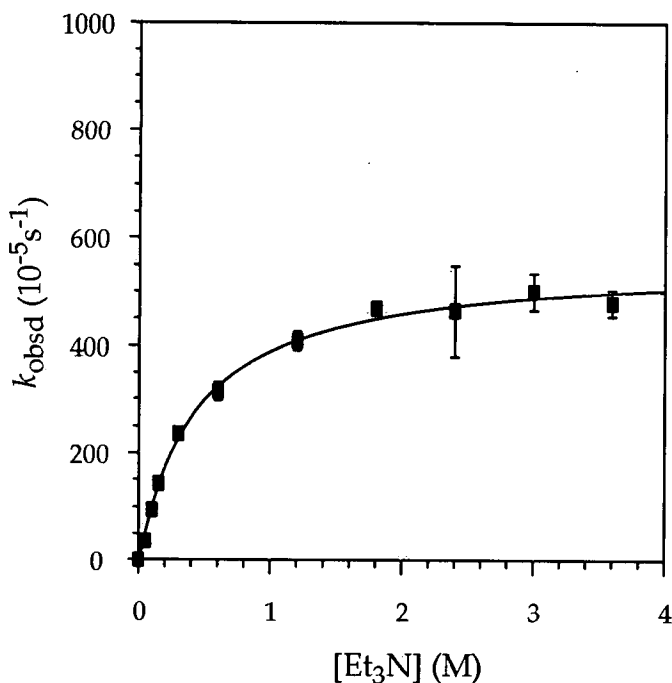


I. Plot of  $k_{\text{obsd}}$  vs [LiHMDS] in toluene for the enolization of **1** (0.004 M) by LiHMDS at  $-40$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{LiHMDS}] + b$  ( $a = -1.1 \pm 0.6 \times 10^{-3}$ ,  $b = 2.0 \pm 0.1 \times 10^{-3}$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

II. Table of data for plot in section I.

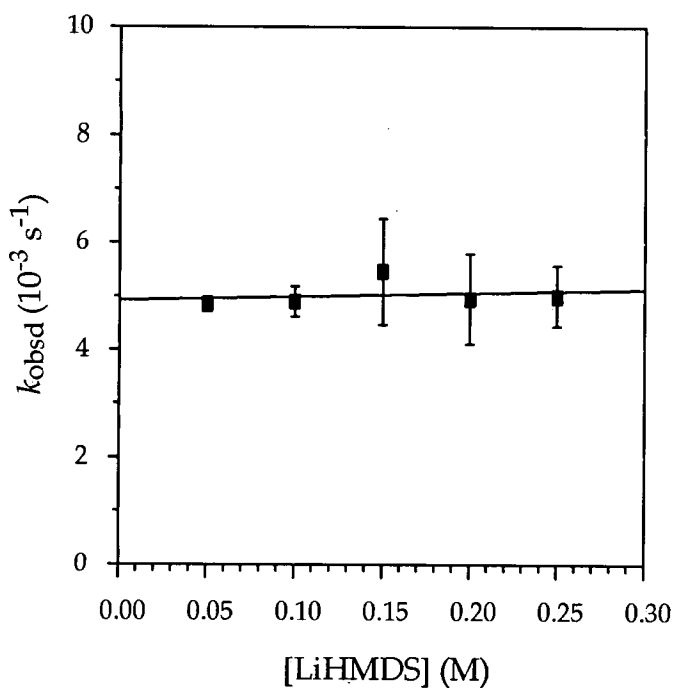
[LiHMDS] (M)	$k_{\text{obsd}1} (\text{s}^{-1})$	$k_{\text{obsd}2} (\text{s}^{-1})$	$k_{\text{obsd}} (\text{avg}) (\text{s}^{-1})$
0.05	$1.76 \pm 0.03\text{E-}3$	$1.95 \pm 0.05\text{E-}3$	$1.8 \pm 0.1\text{E-}3$
0.10	$2.00 \pm 0.03\text{E-}3$	$1.98 \pm 0.02\text{E-}3$	$1.99 \pm 0.01\text{E-}3$
0.15	$1.81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



III. Plot of  $k_{\text{obsd}}$  vs  $[\text{Et}_3\text{N}]$  in toluene cosolvent for the enolization of **1-d<sub>3</sub>** (0.004 M) by LiHMDS (0.10 M) at  $-78$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{Et}_3\text{N}] / (1 + b[\text{Et}_3\text{N}])$  ( $a = 1.25 \pm 0.08 \times 10^{-2}$ ,  $b = 2.2 \pm 0.2$ ).

IV. Table of data for plot in section III.

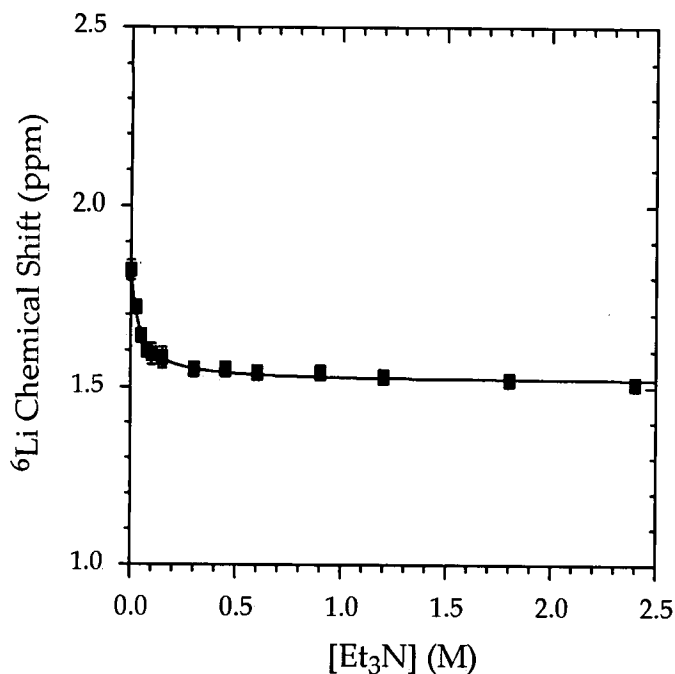
$[\text{Et}_3\text{N}]$ (M)	$k_{\text{obsd}1}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}2}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}(\text{avg})$ ( $\text{s}^{-1}$ )
0.05	$3.8 \pm 0.1\text{E-}4$	$3.4 \pm 0.1\text{E-}4$	$3.6 \pm 0.3\text{E-}4$
0.15	$1.46 \pm 0.02\text{E-}3$	$1.40 \pm 0.02\text{E-}3$	$1.43 \pm 0.04\text{E-}3$
0.30	$2.32 \pm 0.04\text{E-}3$	$2.39 \pm 0.03\text{E-}3$	$2.36 \pm 0.06\text{E-}3$
0.60	$3.02 \pm 0.07\text{E-}3$	$3.2 \pm 0.1\text{E-}3$	$3.1 \pm 0.1\text{E-}3$
1.2	$4.0 \pm 0.2\text{E-}3$	$4.2 \pm 0.1\text{E-}3$	$4.1 \pm 0.1\text{E-}3$
1.8	$4.7 \pm 0.1\text{E-}3$	$4.7 \pm 0.2\text{E-}3$	$4.7 \pm 0.4\text{E-}3$
2.4	$5.0 \pm 0.4\text{E-}3$	$4.2 \pm 0.1\text{E-}3$	$4.6 \pm 0.8\text{E-}3$
3.0	$4.8 \pm 0.2\text{E-}3$	$5.3 \pm 0.2\text{E-}3$	$5.0 \pm 0.3\text{E-}3$
3.6	$4.6 \pm 0.2\text{E-}3$	$5.0 \pm 0.1\text{E-}3$	$4.8 \pm 0.3\text{E-}3$



V. Plot of  $k_{\text{obsd}}$  vs  $[\text{LiHMDS}]$  for the enolization of **1-d<sub>3</sub>** (0.004 M) by LiHMDS in 3.0 M  $\text{Et}_3\text{N}$ /toluene at  $-78^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{LiHMDS}] + b$  ( $a = 2 \pm 3 \times 10^{-3}$ ,  $b = 4.8 \pm 0.4 \times 10^{-4}$ ).

VI. Table of data for plot in section V.

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



VII. Plot of <sup>6</sup>Li chemical shift vs [Et<sub>3</sub>N] for 0.1 M [<sup>6</sup>Li,<sup>15</sup>N]LiHMDS in Et<sub>3</sub>N/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<sup>-1</sup>),  $b = K_{\text{eq}} = 28 \pm 3$  (M<sup>-1</sup>),  $c = 2 \pm 1$ .

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

LiHMDS equiv	$10^5 \cdot k_{\text{obsd}}$ (s <sup>-1</sup> )	
	None <sup>a</sup>	Et <sub>3</sub> N <sup>b</sup>
20	200	410
2.0	510	260
1.0	340	5

<sup>a</sup>Enolizations of **1** (**1-d<sub>0</sub>**) were carried out using 0.1 M LiHMDS in toluene at -40 °C.

<sup>b</sup>Enolizations of **1-d<sub>3</sub>** were carried out using 0.1 M LiHMDS in toluene at -40 °C.

Comparisons across the rows are not valid.