

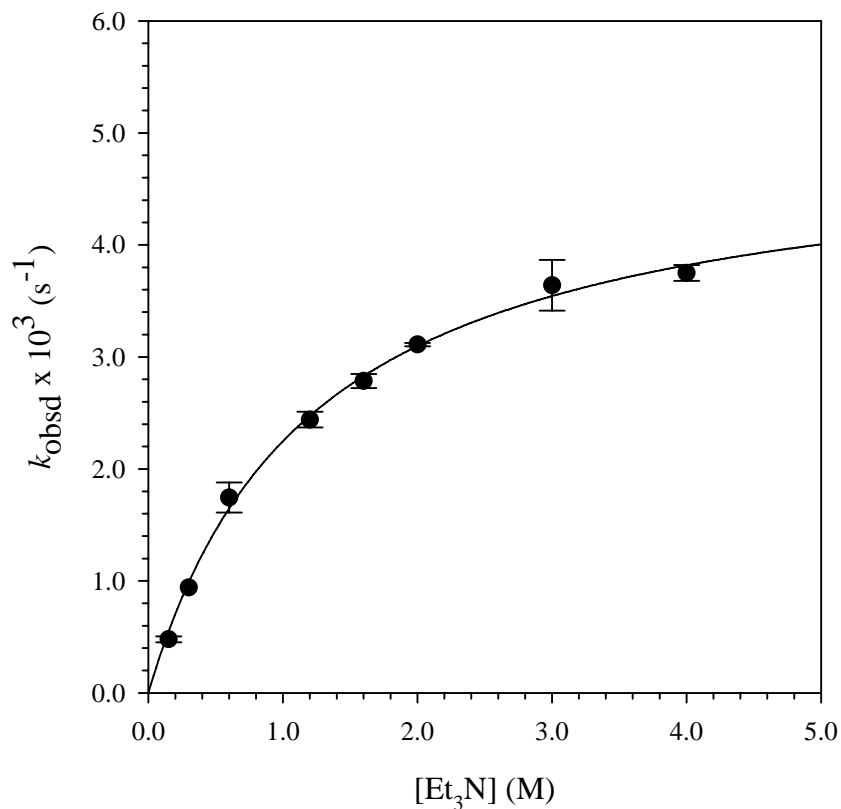
Lithium Hexamethyldisilazide-Mediated Enolizations: Influence of Triethylamine on
E/Z Selectivities and Enolate Reactivities

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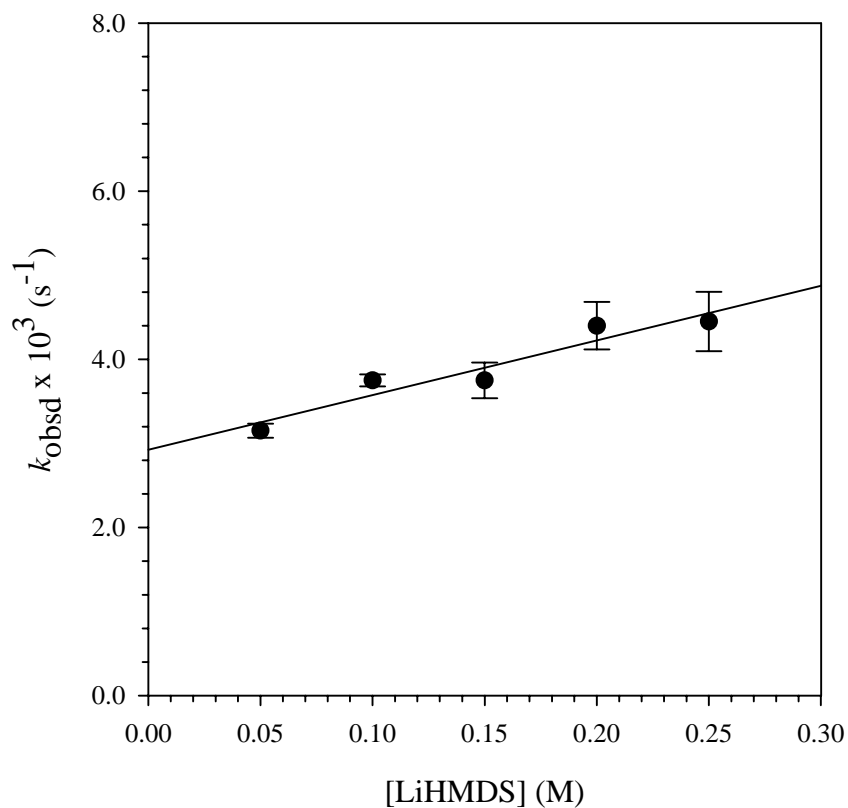
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I. Plot of k_{obsd} vs $[\text{Et}_3\text{N}]$ in toluene for the enolization of **5-d₃** (0.005 M) by LiHMDS (0.10 M) at -78 °C. The line depicts the unweighted least-squares fit to $k_{\text{obsd}} = a[\text{Et}_3\text{N}]/(1 + b[\text{Et}_3\text{N}])$ ($a = 4.0 \pm 0.1$, $b = 8.2 \pm 0.6 \times 10^{-1}$).

II. Table of data for plot in section I.

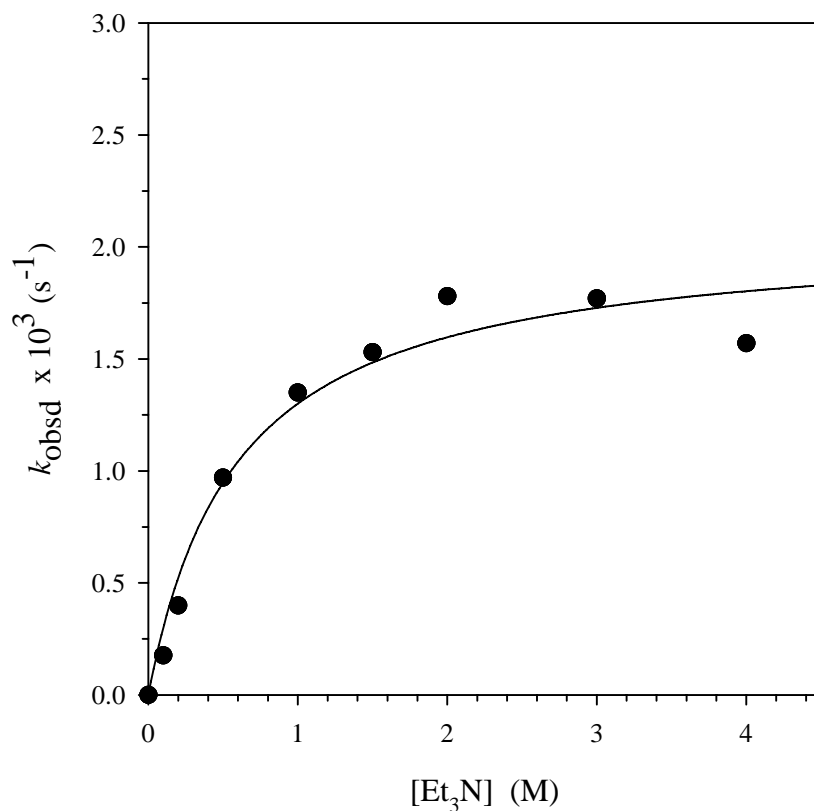
$[\text{Et}_3\text{N}]$ (M)	$k_{\text{obsd}1}$ (s ⁻¹)	$k_{\text{obsd}2}$ (s ⁻¹)	$k_{\text{obsd}}(\text{avg})$ (s ⁻¹)
0.15	$4.97 \pm 0.05\text{E-}4$	$4.60 \pm 0.06\text{E-}4$	$4.7 \pm 0.2\text{E-}4$
0.30	$9.4 \pm 0.1\text{E-}4$	$9.4 \pm 0.1\text{E-}4$	$9.4 \pm 0.0\text{E-}4$
0.60	$1.84 \pm 0.03\text{E-}3$	$1.65 \pm 0.03\text{E-}3$	$1.7 \pm 0.1\text{E-}3$
1.2	$2.49 \pm 0.08\text{E-}3$	$2.39 \pm 0.04\text{E-}3$	$2.44 \pm 0.07\text{E-}3$
1.6	$2.83 \pm 0.06\text{E-}3$	$2.74 \pm 0.07\text{E-}3$	$2.78 \pm 0.06\text{E-}3$
2.0	$3.10 \pm 0.05\text{E-}3$	$3.12 \pm 0.09\text{E-}3$	$3.11 \pm 0.01\text{E-}3$
3.0	$3.48 \pm 0.05\text{E-}3$	$3.8 \pm 0.1\text{E-}3$	$3.6 \pm 0.2\text{E-}3$
4.0	$3.8 \pm 0.1\text{E-}3$	$3.7 \pm 0.1\text{E-}3$	$3.75 \pm 0.07\text{E-}3$



III. Plot of k_{obsd} vs [LiHMDS] for the enolization of **5- d_3** in 4.0 M Et_3N /toluene at -78 °C. The curve depicts the unweighted least-squares fit to $k_{\text{obsd}} = a[\text{LiHMDS}] + b$ ($a = 5 \pm 1 \times 10^{-3}$, $b = 3.0 \pm 0.1 \times 10^{-3}$).

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

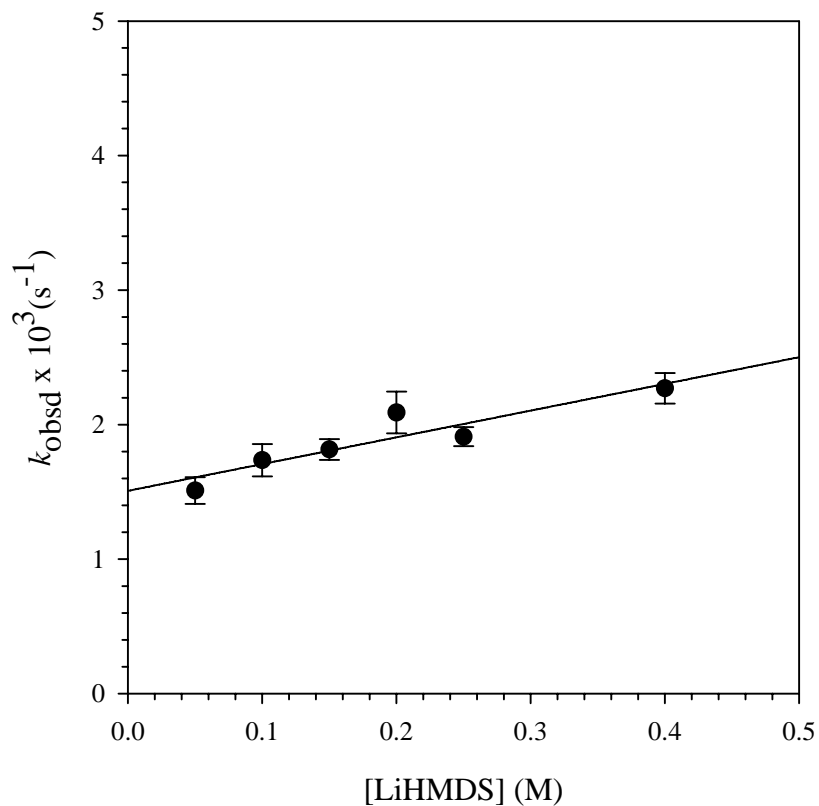
[LiHMDS] (M)	$k_{\text{obsd}1} \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}2} \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}}(\text{avg}) \text{ (s}^{-1}\text{)}$
0.05	$3.21 \pm 0.06\text{E-}3$	$3.09 \pm 0.07\text{E-}3$	$3.15 \pm 0.08\text{E-}3$
0.10	$3.8 \pm 0.1\text{E-}3$	$3.7 \pm 0.1\text{E-}3$	$3.75 \pm 0.07\text{E-}3$
0.15	$3.6 \pm 0.1\text{E-}3$	$3.9 \pm 0.1\text{E-}3$	$3.7 \pm 0.2\text{E-}3$
0.20	$4.2 \pm 0.1\text{E-}3$	$4.6 \pm 0.1\text{E-}3$	$4.4 \pm 0.2\text{E-}3$
0.25	$4.2 \pm 0.1\text{E-}3$	$4.7 \pm 0.1\text{E-}3$	$4.4 \pm 0.3\text{E-}3$



V. Plot of k_{obsd} vs $[\text{Et}_3\text{N}]$ for the enolization of isopropyl propionate by LiHMDS (0.10 M) in toluene at $-78\text{ }^\circ\text{C}$. The curve depicts the unweighted least-squares fit to $k_{\text{obsd}} = a[\text{Et}_3\text{N}]/(1 + b[\text{Et}_3\text{N}])$ ($a = 3.5 \pm 0.6 \times 10^{-3}$, $b = 1.6 \pm 0.4$).

VI. Table of data for plot in section V.

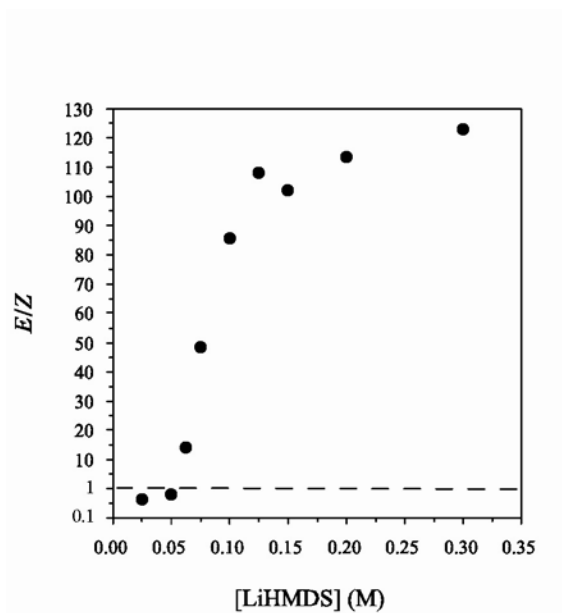
$[\text{Et}_3\text{N}]$ (M)	k_{obsd} (s^{-1})
0.10	$1.76 \pm 0.01\text{E-}4$
0.20	$3.99 \pm 0.02\text{E-}4$
0.50	$9.71 \pm 0.09\text{E-}4$
1.0	$1.35 \pm 0.01\text{E-}3$
1.5	$1.55 \pm 0.02\text{E-}3$
2.0	$1.78 \pm 0.01\text{E-}3$
3.0	$1.77 \pm 0.03\text{E-}3$
4.0	$1.57 \pm 0.01\text{E-}3$



VII. Plot of k_{obsd} vs [LiHMDS] for the enolization of isopropyl propionate in 2.5 M Et_3N /toluene at -78°C . The curve depicts the unweighted least-squares fit to $k_{\text{obsd}} = a[\text{LiHMDS}] + b$ ($a = 1.9 \pm 0.4 \times 10^{-3}$, $b = 1.50 \pm 0.09 \times 10^{-3}$).

VIII. Table of data for the plot in section **VII**.

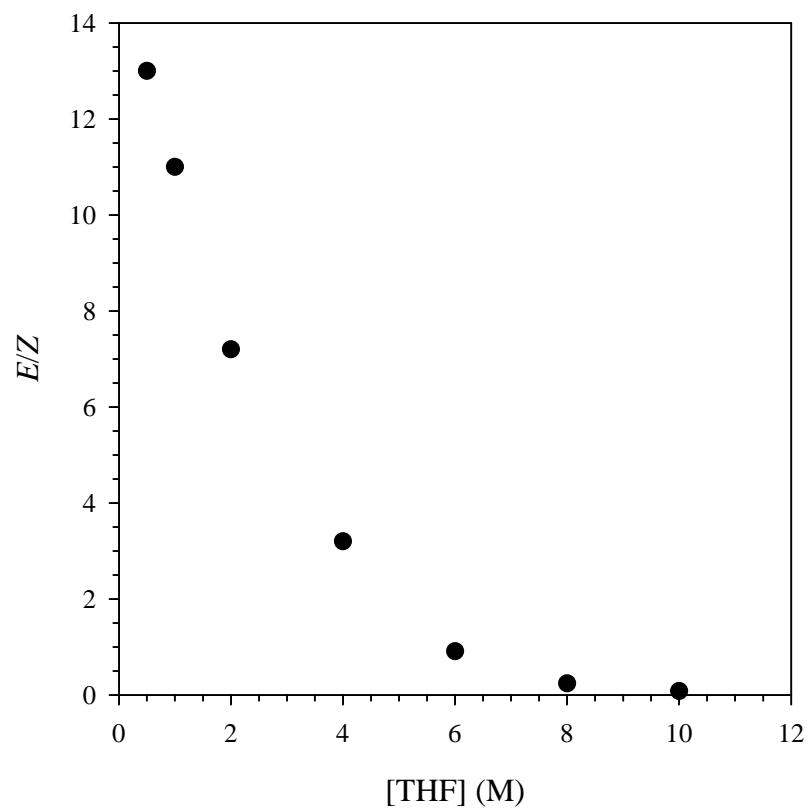
[LiHMDS] (M)	$k_{\text{obsd}1}$ (s^{-1})	$k_{\text{obsd}2}$ (s^{-1})	$k_{\text{obsd}}(\text{avg})$ (s^{-1})
0.05	$1.44 \pm 0.01\text{E-}3$	$1.58 \pm 0.02\text{E-}3$	$1.51 \pm 0.09\text{E-}3$
0.10	$1.82 \pm 0.02\text{E-}3$	$1.65 \pm 0.01\text{E-}3$	$1.7 \pm 0.1\text{E-}3$
0.15	$1.76 \pm 0.02\text{E-}3$	$1.87 \pm 0.01\text{E-}3$	$1.82 \pm 0.07\text{E-}3$
0.20	$2.20 \pm 0.02\text{E-}3$	$1.98 \pm 0.02\text{E-}3$	$2.0 \pm 0.1\text{E-}3$
0.25	$1.86 \pm 0.03\text{E-}3$	$1.96 \pm 0.02\text{E-}3$	$1.91 \pm 0.07\text{E-}3$
0.40	$2.19 \pm 0.03\text{E-}3$	$2.35 \pm 0.03\text{E-}3$	$2.2 \pm 0.1\text{E-}3$



IX. Plot of *E/Z* selectivity for the enolization of **5** (0.05 M) by LiHMDS in 1.5 M Et₃N/toluene at -78 °C.

X. Table of data for the plot in section **IX**.

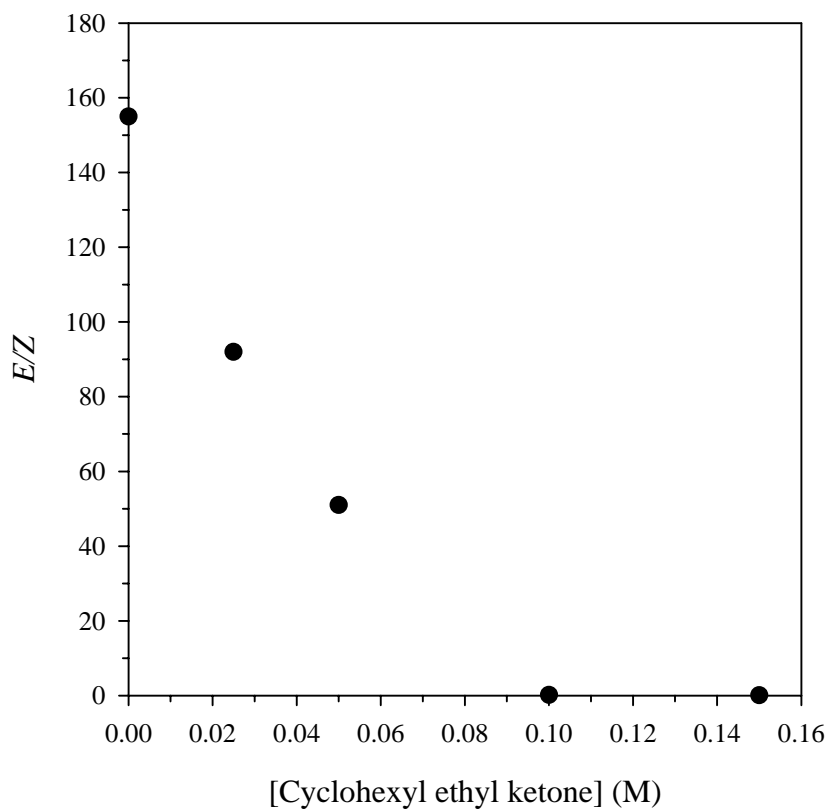
[LiHMDS] (M)	<i>E/Z</i> 1	<i>E/Z</i> 2	<i>E/Z</i> (avg)
0.025	1 : 4.4	1 : 3.2	1 : 3.8
0.05	1 : 2.3	1 : 1.8	1 : 2.1
0.0625	11.4 : 1	16.7 : 1	14 : 1
0.075	49 : 1	48 : 1	49 : 1
0.1	88 : 1	83 : 1	86 : 1
0.125	110 : 1	106 : 1	108 : 1
0.15	106 : 1	98 : 1	102 : 1
0.2	107 : 1	120 : 1	114 : 1
0.3	138 : 1	108 : 1	123 : 1



XI. Plot of *E/Z* selectivity vs. [THF] for the enolization of **5** (0.05 M) by LiHMDS (0.15 M) in toluene at -78 °C.

XII. Table of data for the plot in section **XI**.

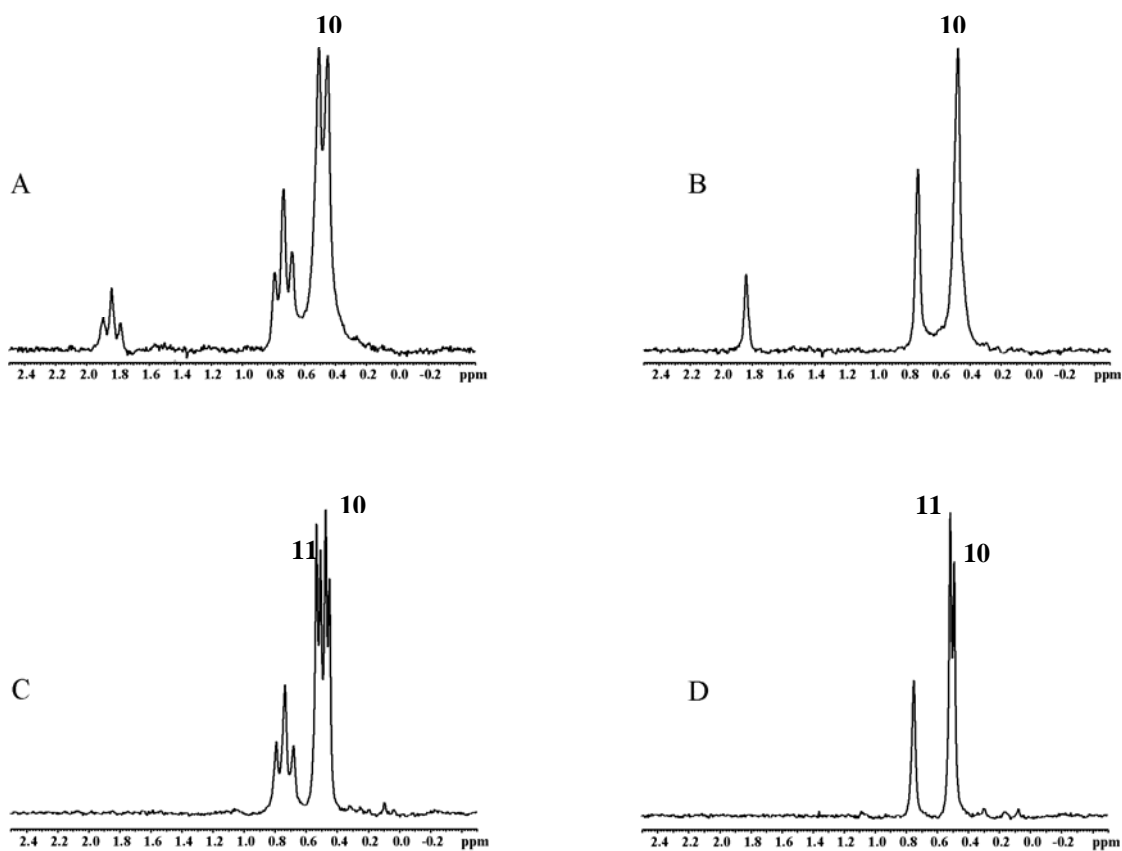
[THF]	<i>E/Z</i>
0.5	13 : 1
1.0	11 : 1
2.0	7.2 : 1
4.0	3.2 : 1
6.0	1 : 1.1
8.0	1 : 4.2
10.0	1 : 13



XIII. Plot of *E/Z* selectivity vs. [cyclohexyl ethyl ketone] for the enolization of **5** (0.05 M) by LiHMDS (0.15 M) in 1.5 M Et₃N/toluene at -78 °C.

XIV. Data for the plot in section **XIII**.

[Cyclohexyl ethyl ketone] (M)	<i>E/Z</i> of 2-methyl-3-pentanone
0	155 : 1
0.025	92 : 1
0.05	51 : 1
0.10	1 : 5
0.15	1 : 10



XV. ${}^6\text{Li}$ spectra recorded on $[\text{}^6\text{Li}, \text{}^{15}\text{N}]\text{LiHMDS}$ (0.15 M), Et_3N (1.5 M), and **5** (0.05 M) in toluene at $-100\text{ }^\circ\text{C}$. (A) Enolization takes place at $-100\text{ }^\circ\text{C}$ showing *E* enolate mixed dimer **10**; (B) Spectrum (A) decoupled; (C) Enolization takes place at $0\text{ }^\circ\text{C}$ showing *E* enolate mixed dimer **10** and *Z* enolate mixed dimer **11**; (D) Spectrum (C) decoupled.

XVI. *E/Z* selectivities for the enolization of **5** (0.05 M) by LiHMDS (0.15 M) in the presence of trialkyl amines at -78 °C in toluene.

Amine	<i>E/Z</i>
Et ₃ N ^a	102 : 1
DMEA ^b	90 : 1
(<i>i</i> -Pr) ₂ EtN ^b	40 : 1
(<i>i</i> -Bu) ₃ N ^b	60 : 1

^a 1.5M ligand. ^b1.0M ligand

XVII. *E/Z* selectivities for the enolization of **5** (0.05 M) by LiHMDS (0.15 M) in the presence of ethereal ligands at -78 °C in toluene.

Ligand	<i>E/Z</i>
THF (0.5 M)	13 : 1
THF (10 M)	1 : 13
2,2,5,5-tetramethyl THF (1.5 M)	42 : 1
cineole (1 M)	38 : 1

XVIII. *E/Z* selectivities for the enolization of **5** (0.05 M) by LiHMDS (0.15 M) in the presence of polydentate ligands at -78 °C in toluene.

Ligand	<i>E/Z</i>
TMEDA	33 : 1
TMCDA	26 : 1
Me ₂ NCH ₂ CH ₂ OMe (1.5 M)	3 : 1
Me ₂ NCH ₂ CH ₂ OMe (0.10 M)	52 : 1

XIX. *E/Z* selectivity of methyl propionate at -78 °C.

lithium amide	ligand	<i>E/Z</i>
LDA	THF	9 : 1
LDA	THF / HMPA	1 : 5
LiHMDS	THF	1 : 8
LiHMDS	Et ₃ N	22 : 1

XX. *E/Z* selectivities for the enolization of various ketones (0.05 M) by LiHMDS (0.15 M) in Et₃N (1.5 M)/toluene at -78 °C. ^a60 °C

ketone	<i>E/Z</i>
3-pentanone	142 : 1
2-methyl-3-pentanone	102 : 1
cyclohexyl ethyl ketone	79 : 1
ethyl phenyl ketone	3.4 : 1

XXI. Stereoselectivities of aldol reaction of ketone enolates (0.05 M) generated by LiHMDS (0.15 M) in Et₃N (1.5 M)/toluene at -78 °C with 0.15 M isobutyraldehyde.

ketone	anti / syn
3-pentanone	8 : 1
2-methyl-3-pentanone	25 : 1
cyclohexyl ethyl ketone	>30 : 1

XXII. Stereoselectivities of aldol reaction of 2-methyl-3-pentanone enolate (0.05 M) generated by LiHMDS (0.15 M) in various enolization and aldol solvent systems at -78 °C with 0.15 M isobutyraldehyde.

enolization solvent	aldol solvent	anti / syn
1.5 M Et ₃ N / toluene	1.5 M Et ₃ N / toluene	25 : 1
1.5 M Et ₃ N / toluene	1.5 M Et ₃ N / 1.5 M THF / toluene	18 : 1
THF	THF	1 : 4

XXIII. Stereoselectivities of aldol reaction of 3-pentanone enolate (0.05 M) generated by LiHMDS (0.15 M) in 1.5 M Et₃N/toluene and various aldol solvent systems at -78 °C with 0.15M isobutyraldehyde.

aldol solvent (1.5 M)	anti / syn
HMPA	1 : 1.5
2,2,5,5-tetramethyl THF	7 : 1
MeOCH ₂ CH ₂ NMe ₂	2.5 : 1
sparteine	2.5 : 1
TMEDA	4 : 1