Structure and Reactivity of Lithium Diisopropylamide Solvated by Polyamines: Evidence of Monomer- and Dimer-Based Dehydrohaloginations

Julius F. Remenar and David B. Collum*
Department of Chemistry, Baker Laboratory
Cornell University
Ithaca, New York 14853-1301

Supporting Information

I. NMR spectra of samples containing 0.10 M [^{6}Li,^{15}N]LDA and 2.0 equiv of PMDTA in aromatic hydrocarbon solvents.

II. NMR spectra of samples containing 0.10 M [^{6}Li,^{15}N]LDA and 0.5 equiv of PMDTA in aromatic hydrocarbon solvents.

III. NMR spectra of samples containing 0.10 M [^{6}Li,^{15}N]LDA and 0.5 equiv of PMDTA in toluene/hexanes mixtures.

IV. NMR spectra of samples containing 0.10 M [^{6}Li]LDA and 0.5 equiv of PMDTA in hexanes at various temperatures.

V. NMR spectra of samples containing 0.15 M [^{6}Li,^{15}N]LDA and 3.4 equiv of PMDTA in hexanes.

VI. NMR spectra of samples containing 0.10 M [^{6}Li]LDA and 0.5-24 equiv of PMDTA at -50 °C.

VII. NMR spectra of samples containing 0.10 M [^{6}Li]LDA and 0.1-1.5 equiv of PMDTA at -70 °C.

VIII. NMR spectra of samples containing 0.10 M [^{6}Li]LDA and 0.1-1.5 equiv of PMDTA at -90 °C.

IX. Plots of k_{obsd} versus [LDA] for samples containing (±)-*exo*-2-halonorbornane (0.004 M) and LDA in solution with 3.0 M TMEDA in toluene at various temperatures.

X. Plots of k_{obsd} versus [LDA] for samples containing (±)-*exo*-2-bromonorbornane (0.004 M) and LDA in solution with 1.0 M PMDTA in hexanes and with 0.1 M free PMDTA in hexanes.

XI. Plots of k_{obsd} versus [ligand] for samples containing (±)-*exo*-2-bromonorbornane (0.004 M) and 0.10 M LDA in solution with various ligands and co-solvents.

XII. Tables of data for plots in Section IX.

XIII. Tables of data for plots in Section X.

XIV. Tables of data for plots in Section XI.

XV. Tables of data for plots in the manuscript.

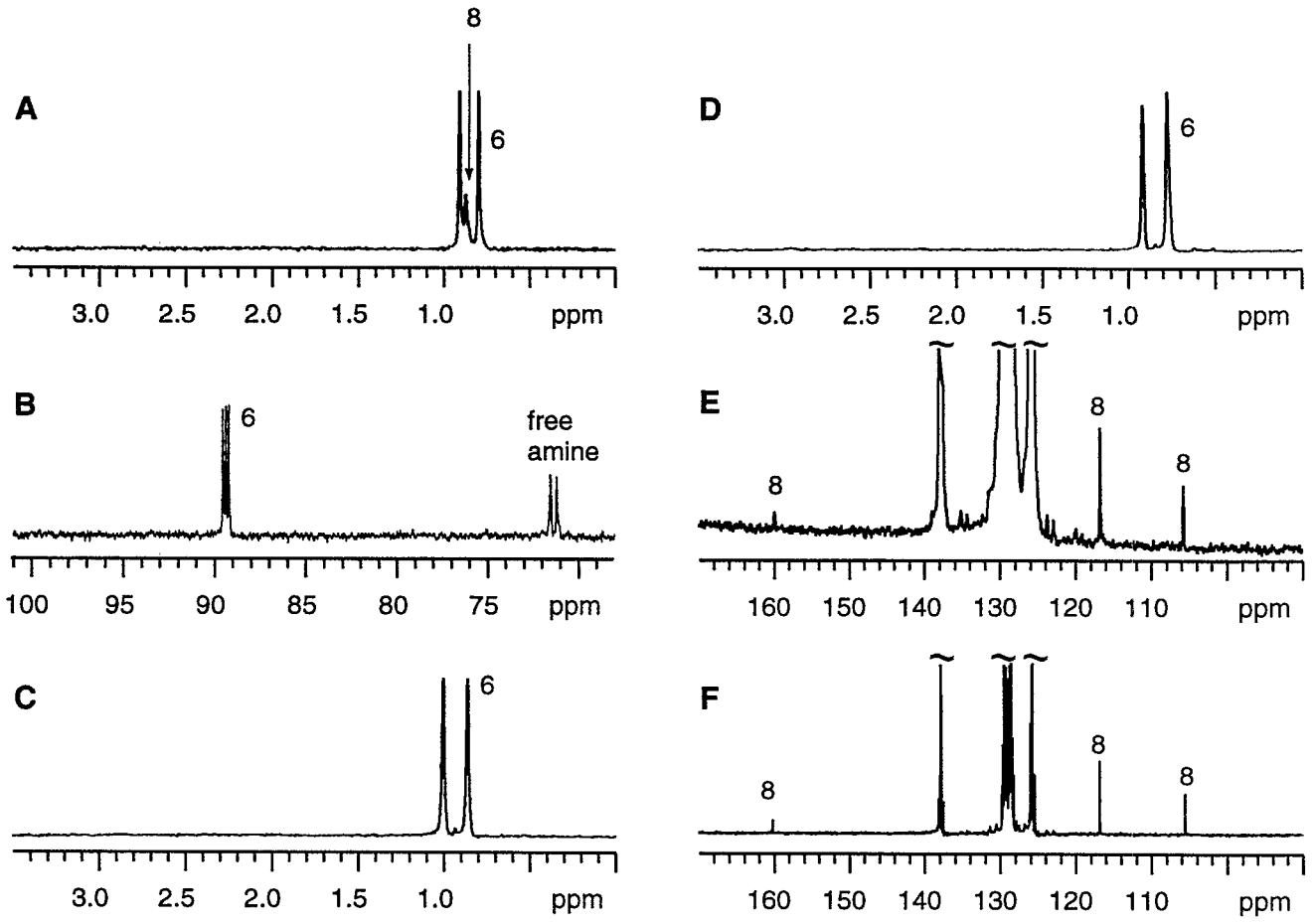

Figure I. NMR spectra of samples containing 2.0 equiv of PMDTA per lithium. (A) ^{6}Li NMR spectrum of 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane; (B) ^{15}N NMR spectrum of 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C; (C) ^{6}Li NMR spectrum of 0.10 M [^{6}Li,^{15}N]LDA in 2:1 cumene:pentane at -90 °C; (D) ^{6}Li NMR spectrum of 0.10 M [^{6}Li,^{15}N]LDA in 2:1 mesitylene:pentane at -90 °C; (E) ^{13}C NMR spectrum of 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -50 °C; (F) ^{13}C NMR spectrum of 0.10 M [^{6}Li]benzyllithium in toluene at -50 °C. The [^{6}Li]benzyllithium was prepared *in situ* by addition of 2 equiv of PMDTA to 0.10 M [^{6}Li]*n*-BuLi in toluene followed by equilibration at RT.

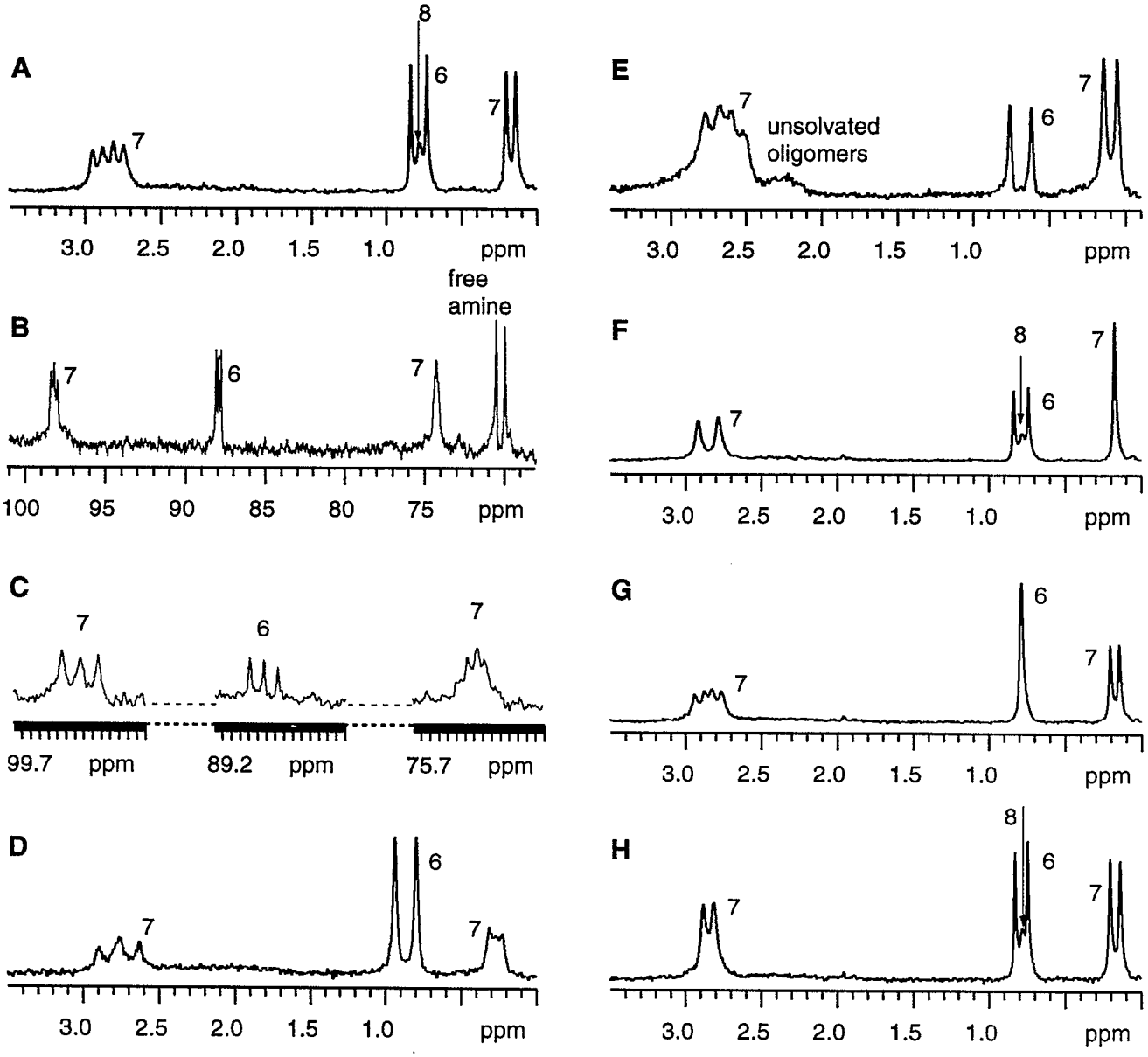

Figure II. NMR spectra of samples containing 0.10 M [^{6}Li,^{15}N]LDA with 0.5 equiv of PMDTA at -105 °C. (A) ^{6}Li NMR spectrum in 2:1 toluene:pentane; (B) ^{15}N NMR spectrum in 2:1 toluene:pentane; (B) ^{15}N NMR spectrum in 2:1 toluene:pentane with multiplets enlarged; (D) ^{6}Li NMR spectrum in 2:1 cumene:pentane; (E) ^{6}Li NMR spectrum in 2:1 mesitylene:pentane; (F) ^{6}Li NMR spectrum in 2:1 toluene:pentane with ^{15}N single-frequency decoupling at 75.7 ppm; (G) ^{6}Li NMR spectrum in 2:1 toluene:pentane with ^{15}N single-frequency decoupling at 89.4 ppm; (H) ^{6}Li NMR spectrum in 2:1 toluene:pentane with ^{15}N single-frequency decoupling at 99.7 ppm.

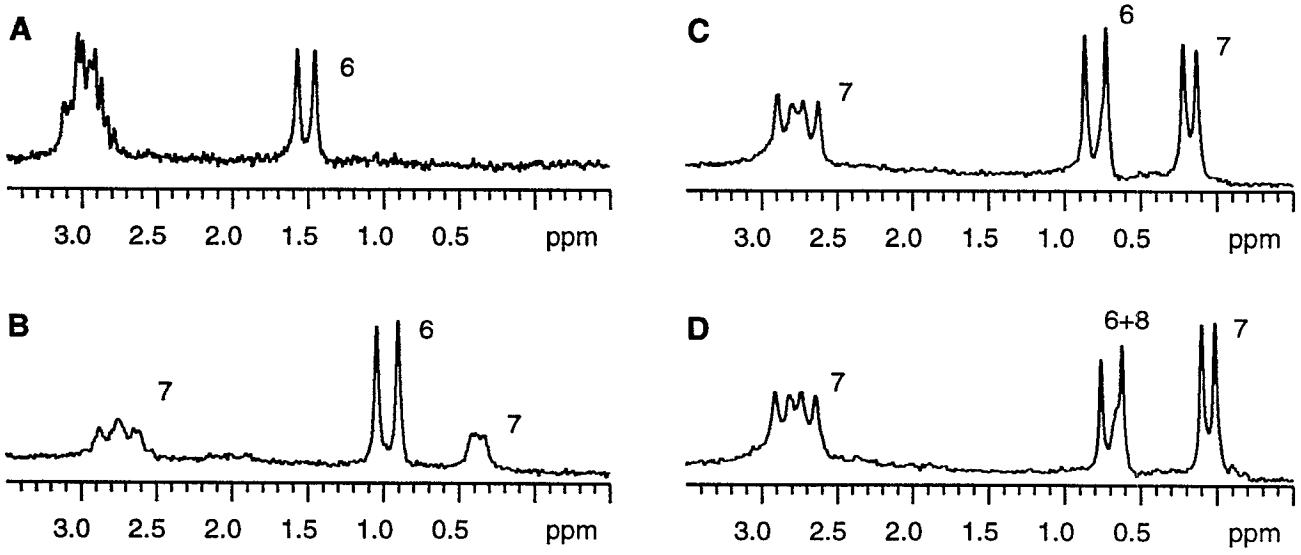

Figure III. ^{6}Li NMR spectra of samples containing 0.10 M [^{6}Li,^{15}N]LDA and 0.50 equiv of PMDTA in hexanes/toluene mixtures. (A) hexanes at -90 °C; (B) 25% toluene in hexanes at -105 °C; (C) 50% toluene in hexanes at -105 °C; (D) 75% toluene in hexanes at -105 °C.

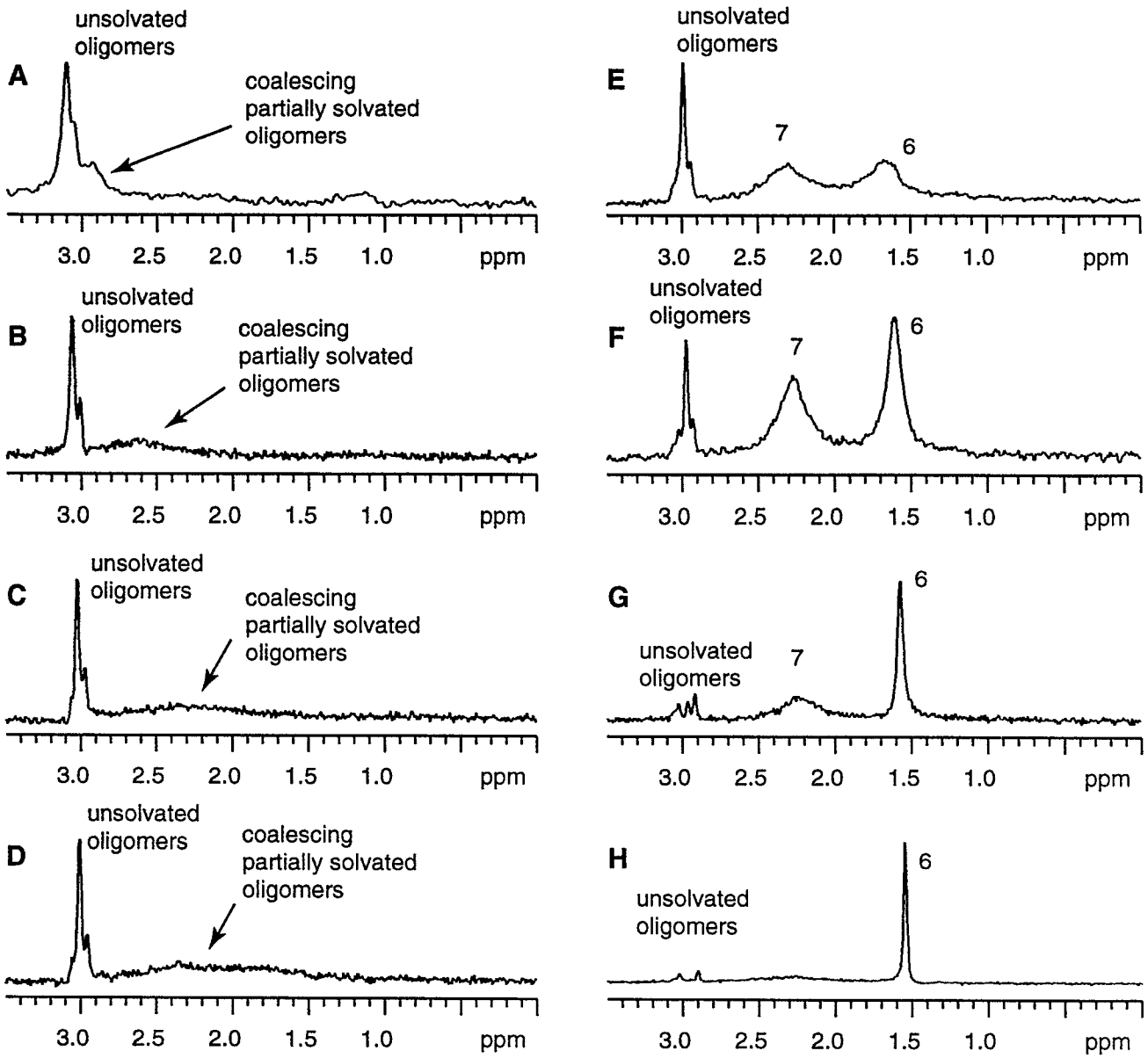

Figure IV. ^{6}Li NMR spectra of samples containing 0.10 M [^{6}Li]LDA and 0.5 equiv of PMDTA in hexanes at various temperatures. (A) 0 °C; (B) -20 °C; (C) -40 °C; (D) -50 °C; (E) -60 °C; (F) -70 °C; (G) -80 °C; (H) -90 °C.

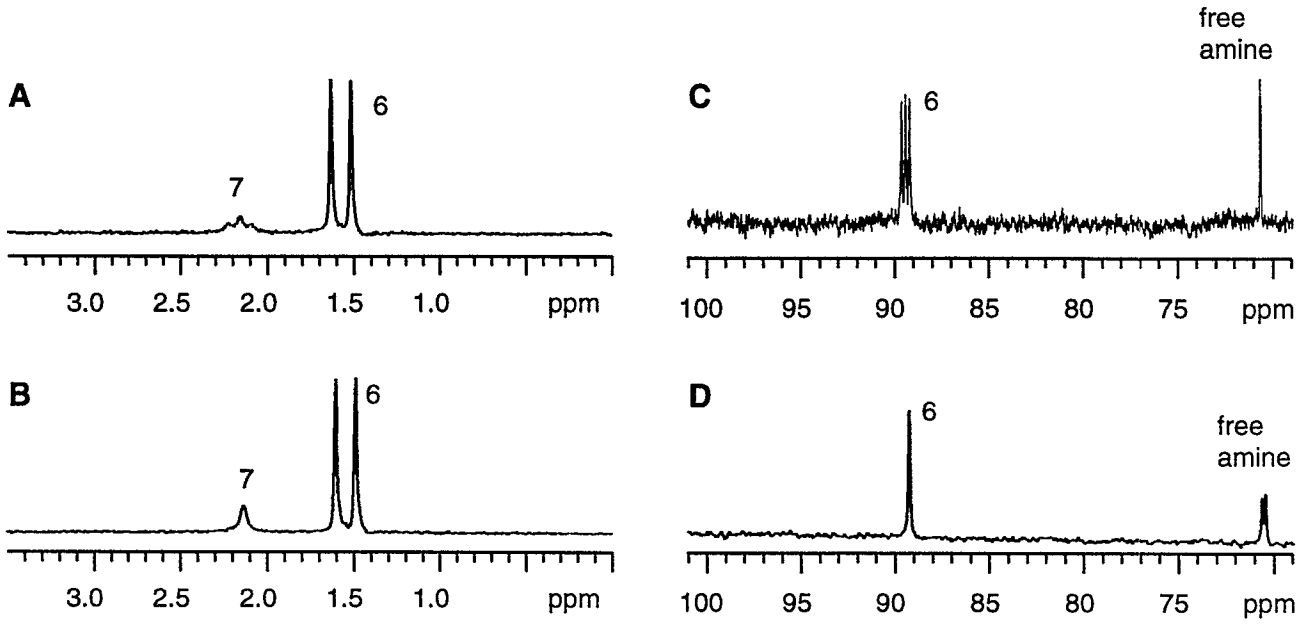

Figure V. NMR spectra of a sample containing 0.15 M [^{6}Li,^{15}N]LDA with 3.5 equiv of PMDTA in pentane at -50 ^{o}C. (A) ^{6}Li NMR spectrum; (B) ^{6}Li NMR spectrum ^{15}N single-frequency decoupling at xx ppm; (C) ^{15}N NMR spectrum; (D) ^{6}Li decoupled ^{15}N NMR spectrum.

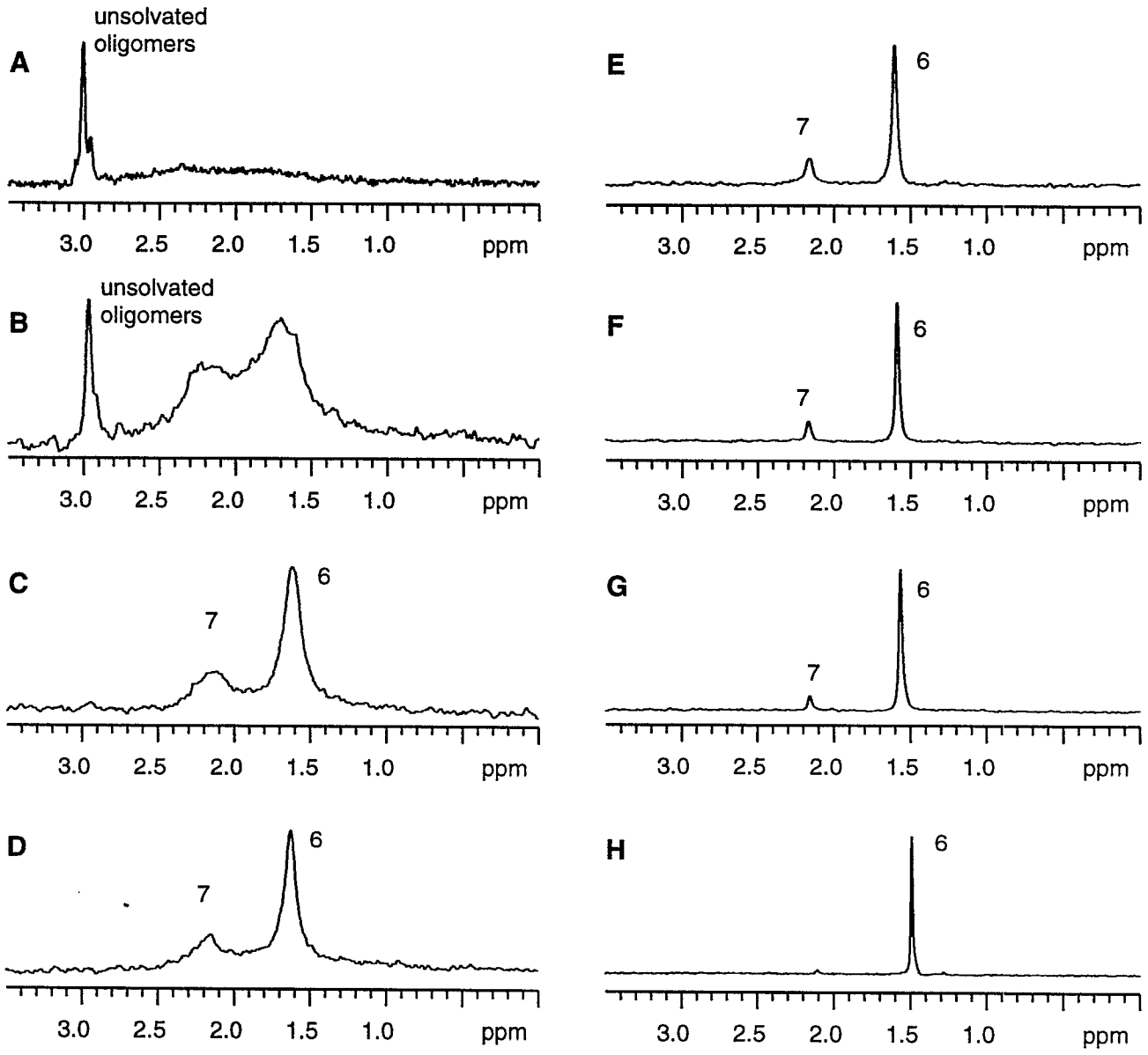

Figure VI. ^{6}Li NMR spectra of samples containing 0.10 M [^{6}Li]LDA in hexanes with various quantities of PMDTA at -50 °C. (A) 0.5 equiv of PMDTA; (B) 0.7 equiv of PMDTA; C) 1.0 equiv of PMDTA; (D) 1.5 equiv of PMDTA; (E) 2.0 equiv of PMDTA; (F) 5.0 equiv of PMDTA; (G) 10 equiv of PMDTA; (H) 24 equiv of PMDTA (50% by volume).

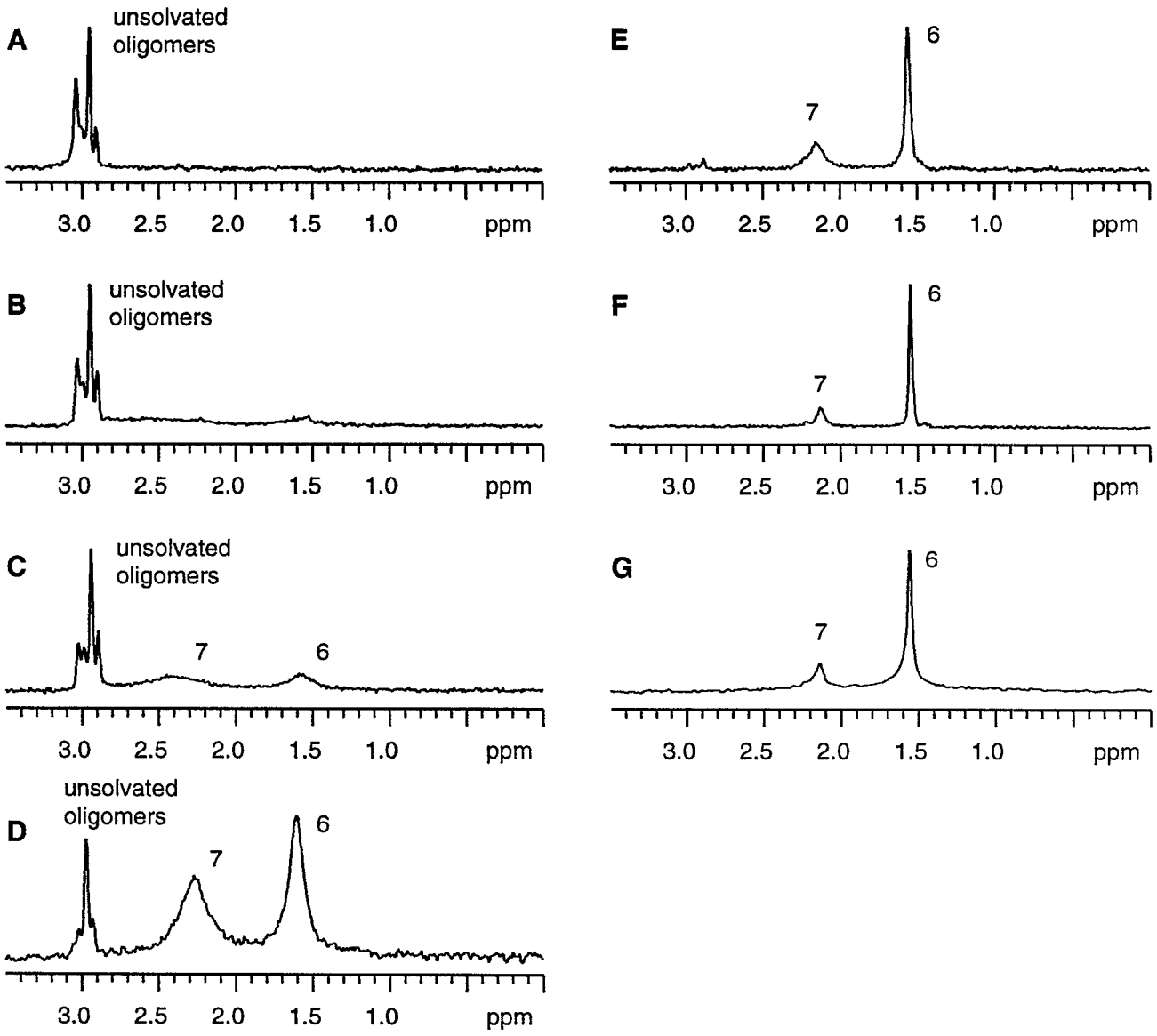

Figure VII. ^{6}Li NMR spectra of samples containing 0.10 M [^{6}Li]LDA in hexanes with various quantities of PMDTA at -70 °C. (A) 0.1 equiv of PMDTA; (B) 0.2 equiv of PMDTA; C) 0.3 equiv of PMDTA; (D) 0.5 equiv of PMDTA; (E) 0.7 equiv of PMDTA; (F) 1.0 equiv of PMDTA; (G) 1.5 equiv of PMDTA.

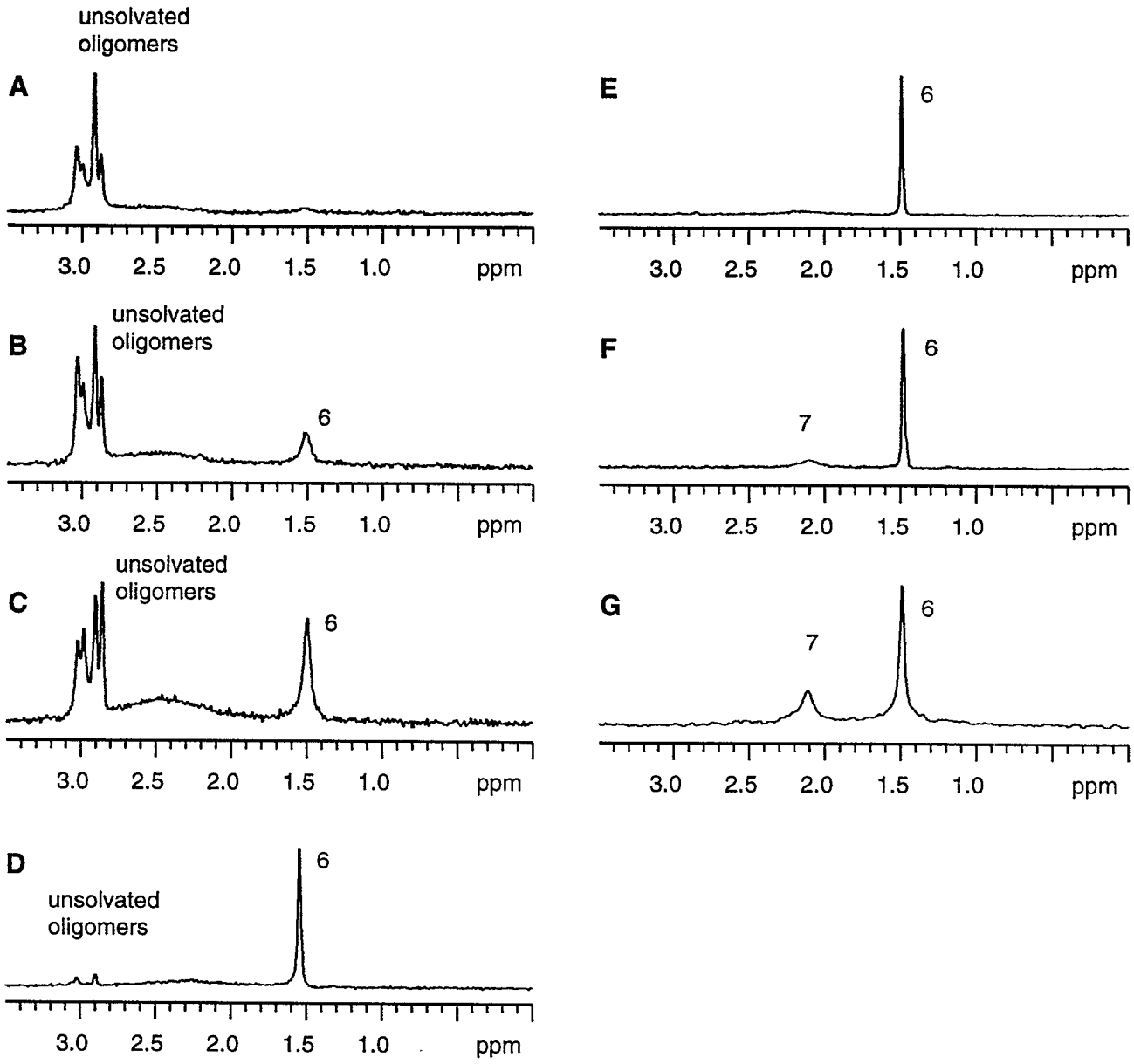

Figure VIII. ^{6}Li NMR spectra of samples containing 0.10 M [^{6}Li]LDA in hexanes with various quantities of PMDTA at -90 °C. (A) 0.1 equiv of PMDTA; (B) 0.2 equiv of PMDTA; C) 0.3 equiv of PMDTA; (D) 0.5 equiv of PMDTA; (E) 0.7 equiv of PMDTA; (F) 1.0 equiv of PMDTA; (G) 1.5 equiv of PMDTA.

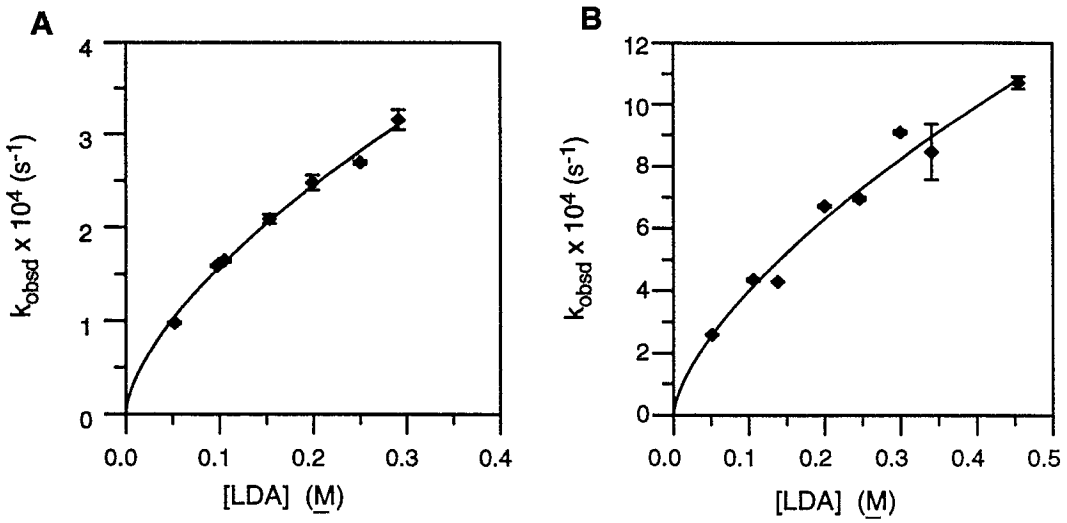

Figure IX. Plots of k_{obsd} versus [LDA] for the elimination of (±)-*exo*-2-halonorbornane (0.004 M) by LDA in solution with 3.0 M TMEDA in toluene. (A) (±)-*exo*-2-bromonorbornane at -60 °C; (B) (±)-*exo*-2-bromonorbornane at -50 °C; (C) (±)-*exo*-2-bromonorbornane at -40 °C; (D) (±)-3,3-dideuterio-*exo*-2-bromonorbornane at -20 °C; (E) (±)-*exo*-2-chloronorbornane at -20 °C; (F) (±)-*exo*-2-chloronorbornane at -20 °C. The curves depict the results of unweighted linear least-squares fits to $f(x) = ax^b$.

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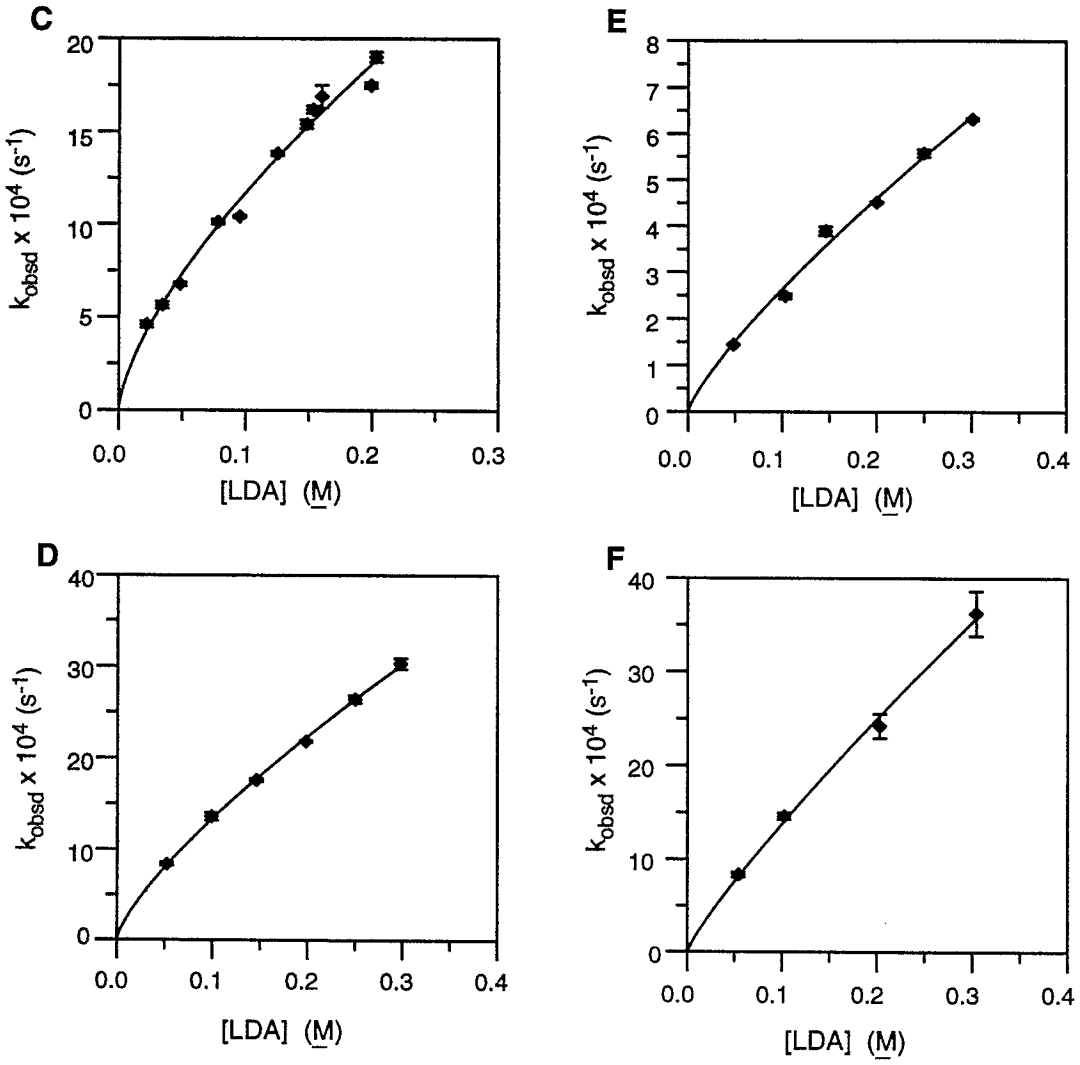
Figure IX (continued)



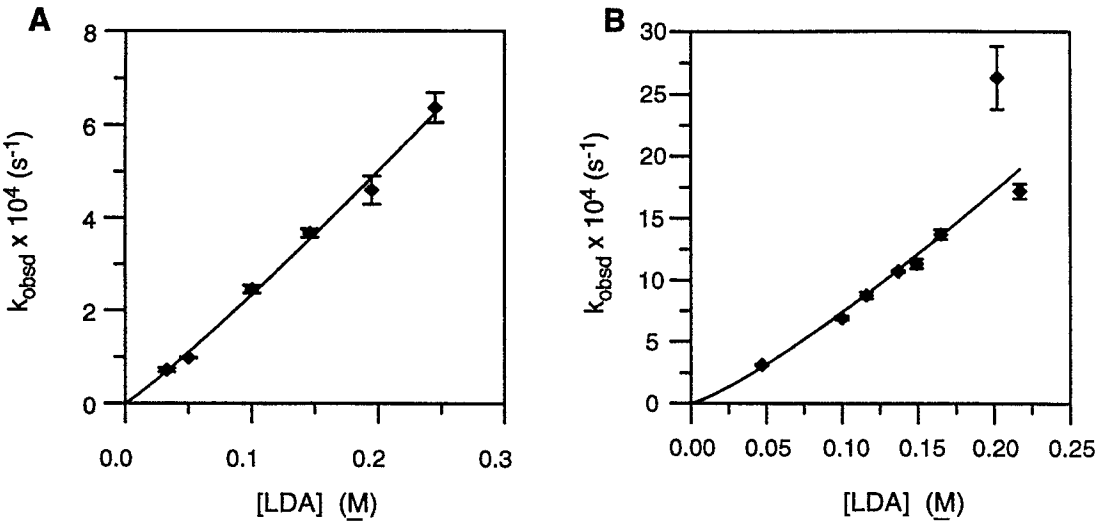


Figure X. Plots of k_{obsd} versus [LDA] for the elimination of (±)-*exo*-2-bromonorbornane (0.004 M) by LDA in solution with PMDTA (in hexanes cosolvent) at -40 °C. (A) 1.0 M PMDTA; (B) 0.10 M plus 1 equiv of PMDTA.

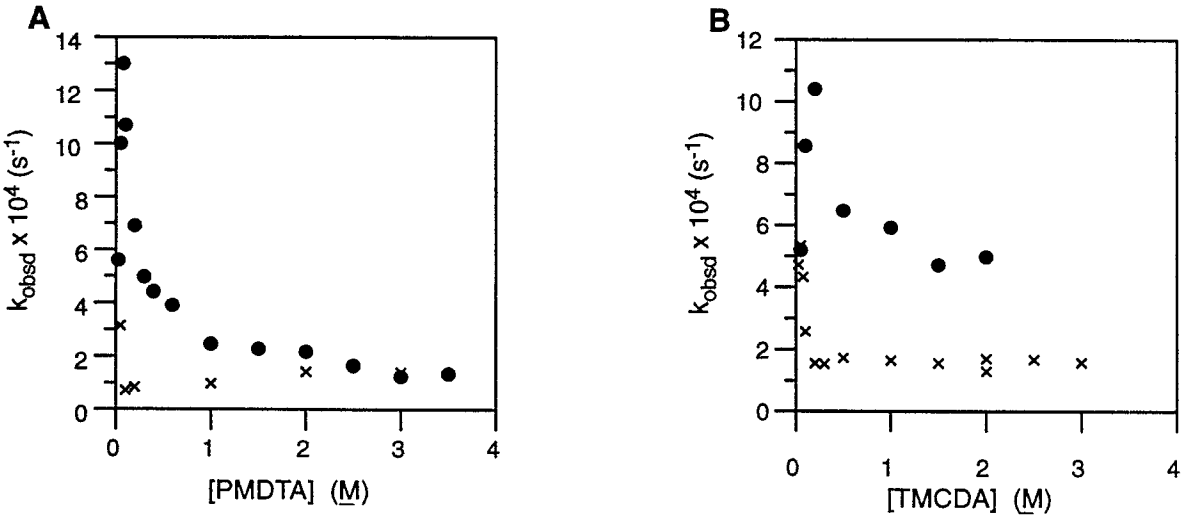


Figure XI. Plots of k_{obsd} versus [ligand] for the elimination of (±)-*exo*-2-bromonorbornane (0.004 M) by 0.10 M LDA in solution at -40 °C. The ligands used were: (A) PMDTA; (B) TMCDA. The (•) symbol represents samples containing hexanes cosolvent, while the (x) symbol represents samples containing toluene cosolvent.

Figure XII. Tables of data for plots in Figure IX.

Data for figure IXA

[LDA] (M)	k_{obsd} (s^{-1})	error
0.052	0.000098	0.000001
0.097	0.000159	0.000001
0.105	0.000165	0.000002
0.153	0.000209	0.000005
0.199	0.000248	0.000008
0.250	0.000270	0.000002
0.291	0.000316	0.000011

Data for figure IXB

[LDA] (M)	k_{obsd} (s^{-1})	error
0.051	0.000259	0.000001
0.106	0.000435	0.000005
0.138	0.000429	0.000001
0.200	0.000671	0.000004
0.246	0.000695	0.000005
0.300	0.000908	0.000005
0.341	0.000845	0.000090
0.455	0.00107	0.000020

Data for figure IXC

[LDA] (M)	k_{obsd} (s^{-1})	error
0.022	0.000459	0.000017
0.034	0.000563	0.000019
0.048	0.000676	0.000010
0.078	0.00101	0.000013
0.095	0.00104	0.000007
0.125	0.00138	0.000012
0.148	0.00154	0.000022
0.153	0.00162	0.000020
0.160	0.00169	0.000061
0.199	0.00175	0.000015
0.203	0.00190	0.000027

Data for figure IXD

[LDA] (M)	k_{obsd} (s^{-1})	error
0.052	0.000837	0.000020
0.099	0.00136	0.000040
0.146	0.00176	0.000020
0.198	0.00218	0.000010
0.250	0.00264	0.000040
0.298	0.00303	0.000060

Figure XII (continued)

Data for figure IXE

[LDA] (M)	k_{obsd} (s^{-1})	error
0.048	0.0001.44	0.000001
0.103	0.0002.49	0.000006
0.146	0.0003.89	0.000009
0.200	0.0004.51	0.000002
0.250	0.0005.57	0.000008
0.301	0.0006.31	0.000003

Data for figure IXF

[LDA] (M)	k_{obsd} (s^{-1})	error
0.054	0.000833	0.000028
0.102	0.00146	0.000035
0.203	0.00242	0.00013
0.304	0.00362	0.00024

Figure XIII. Tables of data for plots in Figure X.

Data for Figure XA

[LDA] (M)	k_{obsd} (s^{-1})	error
0.033	0.000072	0.000004
0.050	0.000098	0.000001
0.100	0.000246	0.000008
0.146	0.000368	0.000009
0.195	0.000460	0.000030
0.245	0.000637	0.000032

Data for Figure XB

[LDA] (M)	k_{obsd} (s^{-1})	error
0.047	0.000312	0.00007
0.100	0.000690	0.00015
0.116	0.000876	0.00028
0.137	0.00107	0.00008
0.149	0.00113	0.00037
0.165	0.00137	0.00040
0.217	0.00172	0.00060
0.202	0.00263	0.00250

Figure XIV. Tables of data for plots in figure XI.

Data for Figure XIA

[PMDTA] (M)	k_{obsd} (s^{-1})	error	cosolvent
0.025	0.000559	0.000014	hexanes
0.050	0.00100	0.000020	hexanes
0.075	0.00130	0.000027	hexanes
0.1	0.00107	0.000030	hexanes
0.20	0.000690	0.000015	hexanes
0.30	0.000497	0.000010	hexanes
0.40	0.000442	0.000009	hexanes
0.60	0.000390	0.000006	hexanes
1.0	0.000246	0.000008	hexanes
1.5	0.000228	0.000003	hexanes
2.0	0.000218	0.000005	hexanes
2.5	0.000160	0.000007	hexanes
3.0	0.000125	0.000006	hexanes
3.5	0.000135	0.000003	hexanes
0.050	0.000314	0.000013	toluene
0.10	0.000072	0.000003	toluene
0.20	0.000084	0.000006	toluene
1.0	0.000098	0.000007	toluene

Data for Figure XIB

[TMCDA] (M)	k_{obsd} (s^{-1})	error	cosolvent
0.025	0.000470	0.000020	toluene
0.05	0.000532	0.000021	toluene
0.075	0.000432	0.000017	toluene
0.10	0.000257	0.000016	toluene
0.20	0.000150	0.000005	toluene
0.30	0.000153	0.000007	toluene
0.50	0.000172	0.000020	toluene
1.0	0.000164	0.000017	toluene
1.5	0.000156	0.000008	toluene
2.0	0.000130	0.000007	toluene
2.0	0.000170	0.000016	toluene
2.5	0.000167	0.000009	toluene
3.0	0.000158	0.000003	toluene
0.050	0.000518	0.00005	hexanes
0.10	0.000856	0.00021	hexanes
0.20	0.00104	0.00040	hexanes
0.50	0.000647	0.00020	hexanes
2.00	0.000496	0.00007	hexanes
1.00	0.000591	0.00010	hexanes
1.50	0.000470	0.00016	hexanes

Figure XV. Tables of data for plots in the manuscript.

Figure XVA. Data for figure 2

[TMEDA] (M)	k_{obsd} (s^{-1})[a]	k_{obsd} (s^{-1})[b]
0.050	0.00189	- - - - - -
0.10	0.00367	0.00135
0.15	0.00320	- - - - - -
0.20	0.00271	0.00206
0.25	0.00230	- - - - - -
0.30	0.00197	0.00229
0.40	0.00160	0.00245
0.50	0.00162	0.00239
0.70	0.00134	0.00220
1.0	0.00123	0.00194
1.5	0.00113	0.00179
2.0	0.00107	0.00151
2.5	0.00102	0.00127
3.0	0.00099	0.00118
3.5	0.00102	- - - - - -
4.0	0.00099	- - - - - -

[a]elimination of (±)-*exo*-2-bromonorbornane at -40 °C. [b]elimination of (±)-*exo*-2-chloronorbornane at 0 °C.

Figure XVB. Data for figure 3

[PMDTA] (M)	k_{obsd} (s^{-1})	error
0.025	0.000559	0.000014
0.050	0.00100	0.000020
0.075	0.00130	0.000027
0.1	0.00107	0.000030
0.20	0.000690	0.000015
0.30	0.000497	0.000010
0.40	0.000442	0.000009
0.60	0.000390	0.000006
1.0	0.000246	0.000008
1.5	0.000228	0.000003
2.0	0.000218	0.000005
2.5	0.000160	0.000007
3.0	0.000125	0.000006
3.5	0.000135	0.000003

Figure XV (continued)

Figure XVC. Data for figure 4

[LDA] (M)	k_{obsd} (s^{-1})	error
0.049	0.0000707	0.000002
0.100	0.000130	0.000005
0.140	0.000202	0.000008
0.194	0.000288	0.000004
0.271	0.000391	0.000003

Figure XVD. Data for figure 5

[TMCDA] (M)	k_{obsd} (s^{-1})	error
0.025	0.000470	0.000020
0.05	0.000532	0.000021
0.075	0.000432	0.000017
0.10	0.000257	0.000016
0.20	0.000150	0.000005
0.30	0.000153	0.000007
0.50	0.000172	0.000020
1.0	0.000164	0.000017
1.5	0.000156	0.000008
2.0	0.000130	0.000007
2.0	0.000170	0.000016
2.5	0.000167	0.000009
3.0	0.000158	0.000003

Figure XVE. Data for figure 6

[LDA] (M)	k_{obsd} (s^{-1})	error
0.027	0.000598	0.000020
0.040	0.000727	0.000010
0.075	0.00164	0.000060
0.121	0.00231	0.000100
0.150	0.00351	0.000180
0.175	0.00394	0.000300