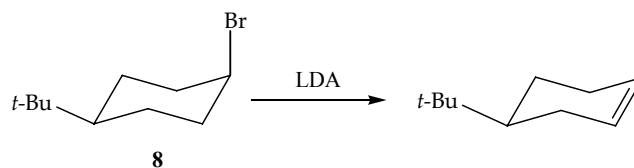


Lithium Diisopropylamide Solvated by Hexamethylphosphoramide:
Substrate-Dependent Mechanisms for Dehydrobrominations

Yun Ma, Antonio Ramírez, Kanwal Jit Singh, Ivan Keresztes
and David B. Collum*

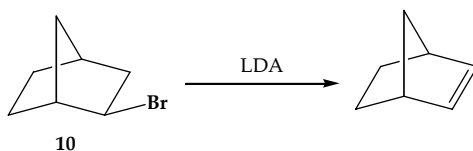
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Supporting Information

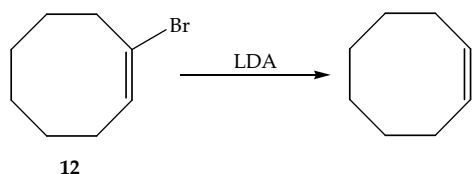


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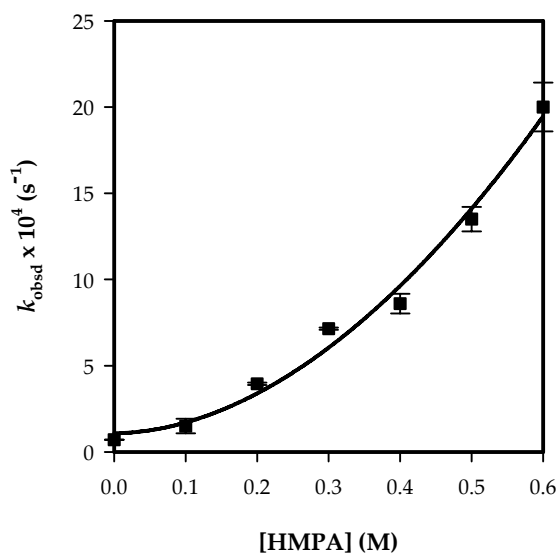


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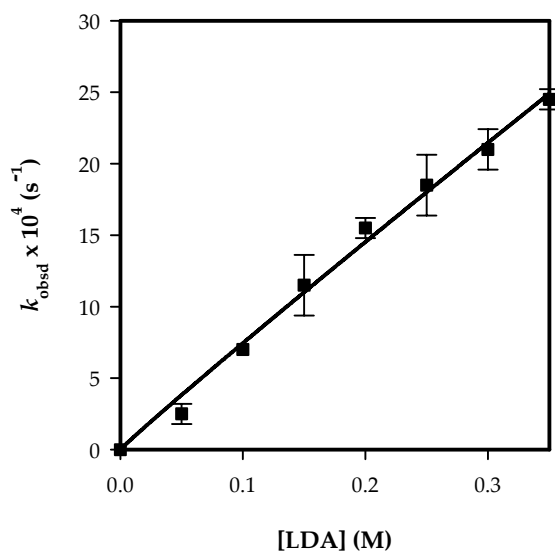
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I. Plot of k_{obsd} vs $[\text{HMPA}]$ for the dehydrobromination of *cis*-1-bromo-4-*tert*-butylcyclohexane **8** (0.004 M) by LDA (0.10 M) in THF (10.0 M)/hexane at $-55\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{HMPA}]^n + k'$ ($k = 4.8 \pm 0.7 \times 10^{-3}$, $k' = 1.0 \pm 0.7 \times 10^{-4}$, $n = 1.9 \pm 0.2$).

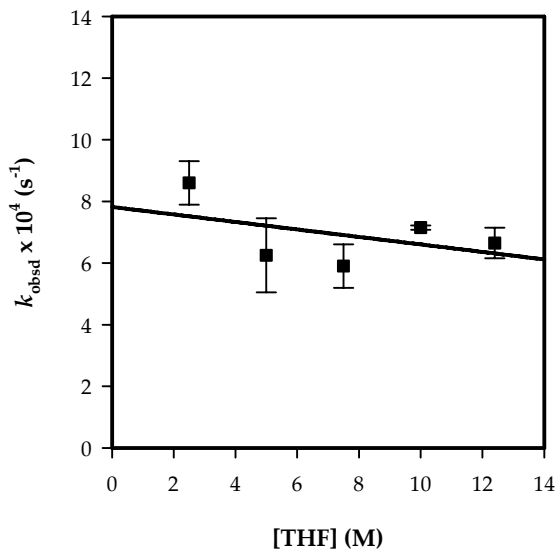
$[\text{HMPA}] \text{ (M)}^{\text{a}}$	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^4 \text{ (s}^{-1}\text{)}$
0.00	0.70 ± 0.01	0.72 ± 0.04	0.71 ± 0.1
0.10	1.2 ± 0.1	1.8 ± 0.1	1.5 ± 0.4
0.20	3.9 ± 0.2	4.0 ± 0.2	4.39 ± 0.07
0.30	7.2 ± 0.1	7.1 ± 0.1	7.15 ± 0.07
0.40	9.0 ± 0.1	8.2 ± 0.1	8.6 ± 0.6
0.50	13.0 ± 0.2	14.0 ± 0.1	13.5 ± 0.7
0.60	21.0 ± 0.2	19.0 ± 0.1	20 ± 1

^a $[\text{HMPA}]$ refers to the concentration of free (uncoordinated) HMPA.



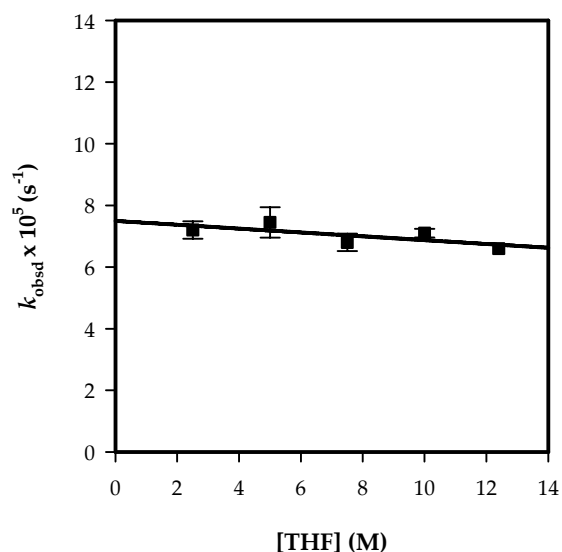
II. Plot of k_{obsd} vs [LDA] for the dehydrobromination of *cis*-1-bromo-4-*tert*-butylcyclohexane **8** (0.004 M) in 0.30 M free HMPA/THF (10.0 M)/hexane at -55 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LDA}]^n + k'$ ($k = 6.7 \pm 0.8 \times 10^{-3}$, $k' = 4.5 \pm 0.3 \times 10^{-4}$, $n = 0.96 \pm 0.09$).

[LDA] (M)	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^4 \text{ (s}^{-1}\text{)}$
0.05	3.0 ± 0.1	2.0 ± 0.1	2.5 ± 0.7
0.10	7.0 ± 0.1	7.0 ± 0.1	7.0 ± 0.0
0.15	10.0 ± 0.1	13.0 ± 0.1	12 ± 2
0.20	15.0 ± 0.1	16.0 ± 0.1	15.5 ± 0.7
0.25	17.0 ± 0.1	20.0 ± 0.1	19 ± 2
0.30	20.0 ± 0.2	22.0 ± 0.2	21 ± 1
0.35	24.0 ± 0.4	25.0 ± 0.4	24.5 ± 0.7



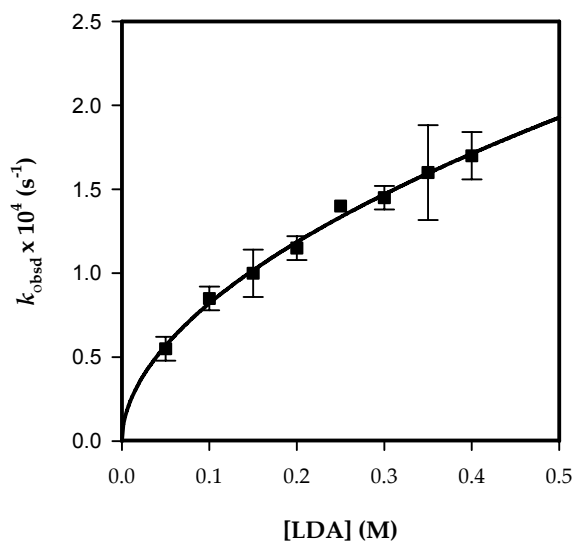
III. Plot of k_{obsd} vs [THF] for the dehydrobromination of *cis*-1-bromo-4-*tert*-butylcyclohexane **8** (0.004 M) by 0.10 M LDA in 0.30 M free HMPA/hexane at -55 °C. The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}] + k'$ ($k = -1.1 \pm 0.1 \times 10^{-4}$, $k' = 7.6 \pm 0.7 \times 10^{-4}$)

[THF] (M)	$k_{\text{obsd1}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd2}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd}} (\text{av}) \times 10^4$ (s ⁻¹)
2.5	8.1 ± 0.1	9.1 ± 0.2	8.6 ± 0.7
5.0	7.1 ± 0.1	5.4 ± 0.1	6 ± 1
7.5	6.4 ± 0.2	5.4 ± 0.1	5.5 ± 0.7
10.0	7.2 ± 0.1	7.1 ± 0.1	7.15 ± 0.1
11.6	6.3 ± 0.2	7.0 ± 0.1	6.7 ± 0.5



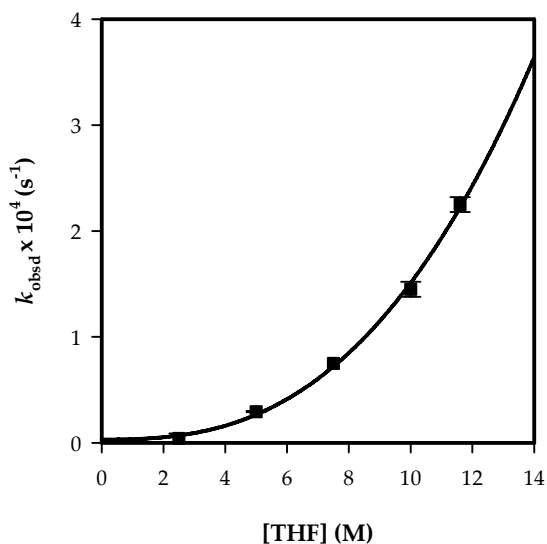
IV. Plot of k_{obsd} vs [THF] for the dehydrobromination of *cis*-1-bromo-4-*tert*-butylcyclohexane **8** (0.004 M) by 0.10 M LDA in 1.0 equiv HMPA (no free HMPA) /hexane at -55 °C. The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}] + k'$ ($k = -6.0 \pm 0.6 \times 10^{-5}$, $k' = 7.5 \pm 0.73 \times 10^{-3}$)

[THF] (M)	$k_{\text{obsd1}} \times 10^5 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^5 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^5 \text{ (s}^{-1}\text{)}$
2.5	7.0 ± 0.3	7.4 ± 0.2	7.2 ± 0.3
5.0	7.8 ± 0.1	7.1 ± 0.1	7.5 ± 0.5
7.5	6.6 ± 0.2	7.0 ± 0.4	6.8 ± 0.3
10.0	7.2 ± 0.2	7.0 ± 0.3	7.1 ± 0.1
11.8	6.6 ± 0.2	6.6 ± 0.2	6.6 ± 0.0



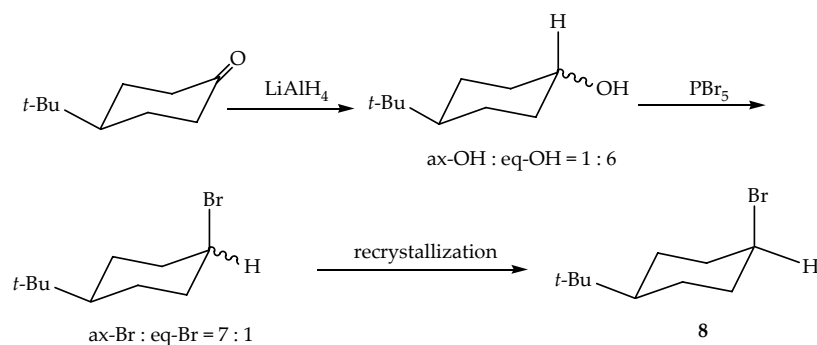
V. Plot of k_{obsd} vs [LDA] for the dehydrobromination of *cis*-1-bromo-4-*tert*-butylcyclohexane **8** (0.004 M) in THF (10.0 M)/hexane at 20 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LDA}]^n$ ($k = 2.7 \pm 0.1 \times 10^{-4}$, $n = 0.50 \pm 0.02$).

[LDA] (M)	$k_{\text{obsd1}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd2}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd}} (\text{av}) \times 10^4$ (s ⁻¹)
0.05	0.50 ± 0.01	0.60 ± 0.01	0.55 ± 0.07
0.10	0.90 ± 0.01	0.80 ± 0.01	0.85 ± 0.07
0.15	1.1 ± 0.1	0.90 ± 0.02	1.0 ± 0.1
0.20	1.2 ± 0.1	1.1 ± 0.1	1.15 ± 0.07
0.25	1.4 ± 0.1	1.4 ± 0.2	1.4 ± 0.0
0.30	1.5 ± 0.1	1.4 ± 0.2	1.45 ± 0.07
0.35	1.8 ± 0.2	1.4 ± 0.1	1.6 ± 0.3
0.40	1.6 ± 0.1	1.8 ± 0.2	1.7 ± 0.6



VI. Plot of k_{obsd} vs $[\text{THF}]$ for the dehydrobromination of *cis*-1-bromo-4-*tert*-butylcyclohexane **8** (0.004 M) by 0.30 M LDA in hexane at 20 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}]^n + k'$ ($k = 1.0 \pm 0.2 \times 10^{-6}$, $k' = 3.0 \pm 0.3 \times 10^{-7}$, $n = 2.2 \pm 0.1$).

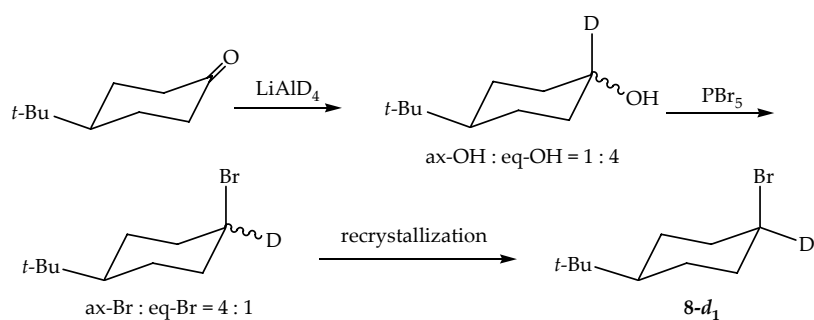
$[\text{THF}] \text{ (M)}$	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^4 \text{ (s}^{-1}\text{)}$
2.5	0.08 ± 0.01	0.10 ± 0.02	0.09 ± 0.01
5.0	0.30 ± 0.01	0.29 ± 0.01	0.30 ± 0.01
7.5	0.75 ± 0.02	0.75 ± 0.01	0.75 ± 0.02
10.0	1.5 ± 0.1	1.4 ± 0.1	1.45 ± 0.07
12.2	2.2 ± 0.2	2.3 ± 0.1	2.25 ± 0.07



VII. Synthesis of *cis*-1-bromo-4-*tert*-butylcyclohexane **8**

(See Eliel, E. L.; Haber, R. G. *J. Org. Chem.* **1959**, *24*, 143.)

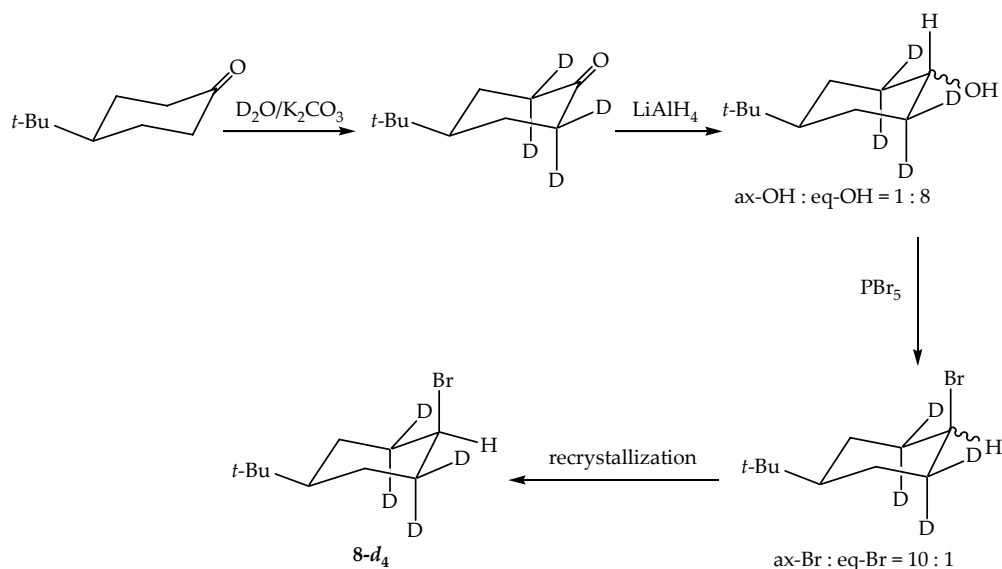
^1H NMR (400 MHz, CDCl_3) δ 4.70 (1H, m), 2.12 (2H, m), 1.76 (2H, m), 1.60 (4H, m), 1.04 (1H, m), 0.89 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 47.7, 35.3, 32.6, 27.4, 21.7.



VIII. Synthesis of *cis*-1-bromo-1-deuterio-4-*tert*-butylcyclohexane **8-d₁**

(See Eliel, E. L.; Haber, R. G. *J. Org. Chem.* **1959**, *24*, 143.)

^1H NMR (400 MHz, CDCl_3) δ 2.15 (2H, m), 1.75 (2H, m), 1.61 (4H, m), 1.01 (1H, m), 0.86 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 47.7, 35.1, 32.6, 27.4, 21.7; MS m/z 163, 140, 124, 82, 57.



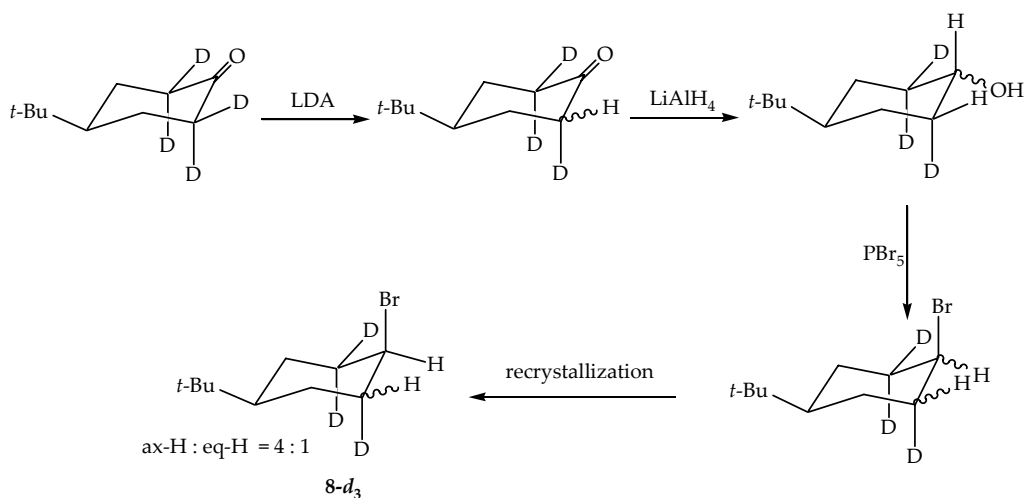
IX. Synthesis of *cis*-1-bromo-2,2,5,5-tetradeuterio-4-*tert*-butylcyclohexane **8-d₄**

4-*tert*-Butylcyclohexanone 2,2,5,5-*d*₄ was prepared by treatment of 4-*tert*-butylcyclohexanone (35.0 g, 230 mmol) with D₂O (20.0 mL) in the presence of K₂CO₃ (5.0 g) in toluene (10.0 mL). The mixture was refluxed for 12 h. Toluene was used to prevent the reaction from crystallizing in the condenser during reflux. The mixture was extracted with pentane (3 x 20 mL) and dried by Na₂SO₄. The solvent was removed in vacuo. Three such treatments were carried out to give (31.2 g, 87% yield) of the product, which was > 98% deuterated according to ¹H NMR and mass spectra.

4-*tert*-Butylcyclohexanol-2,2,5,5-*d*₄ was prepared by treatment of the ketone with LiAlH₄ to give (29.0 g, 92% yield) as a mixture. (See Lambert, J. B.; Emblidge, R. W. and Malany, S. *J. Am. Soc. Chem.* **1993**, *115*, 1317.)

cis-1-Bromo-2,2,5,5-tetradeuterio-4-*tert*-butylcyclohexane: To an oven-dried, round-bottomed, three-necked 300 mL flask fitted with a thermometer, a septum, and a mechanical stirrer was added triphenylphosphine (17.5 g, 66.8 mmol) and methylene chloride (75.0 mL). Bromine (3.4 mL, 66.8 mmol) was added by syringe over 10 min to the rapidly stirred mixture. A cold water-bath was used to keep the reaction mixture between 20 and 30 °C. Solid *trans*-1-hydroxy-2,2,5,5-tetradeuterio-4-*tert*-butylcyclohexane (10.0 g, 63.0 mmol) was added in one portion. The yellow reaction mixture became homogeneous. The reaction was complete after 2 h. Ice water (200.0 g) was added and stirring continued for an additional 1 h to decompose the phosphorus halides. The organic phase was then washed with water, sodium bicarbonate solution, and brine. The solvent

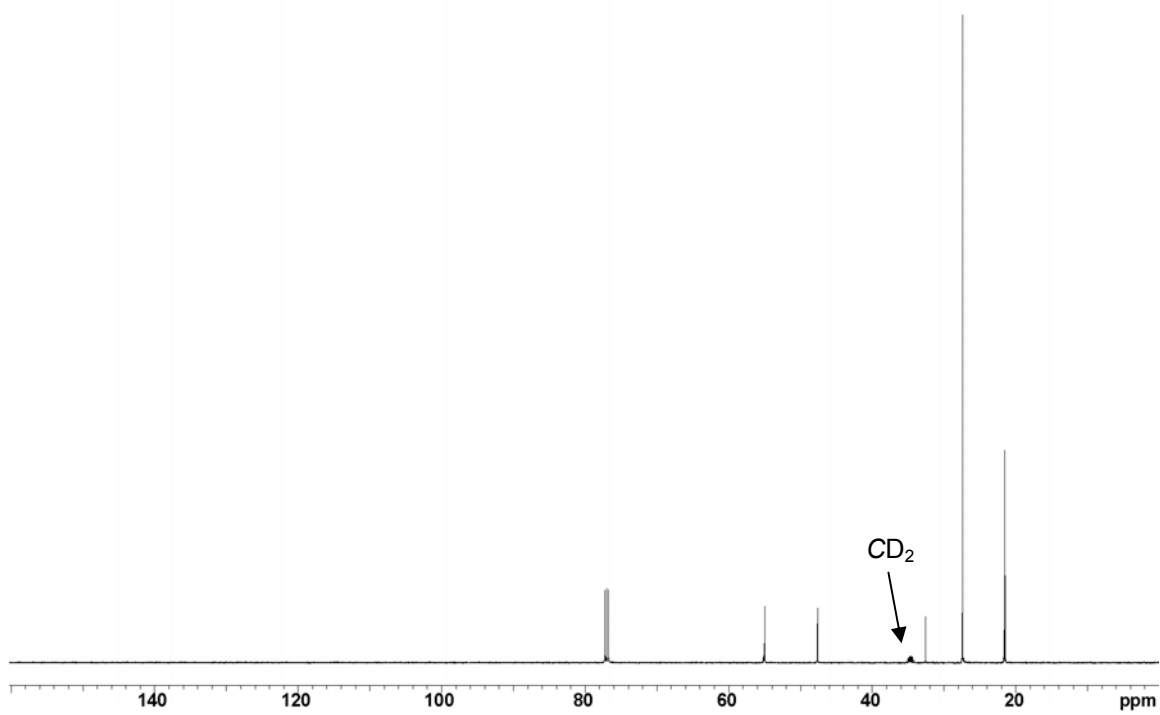
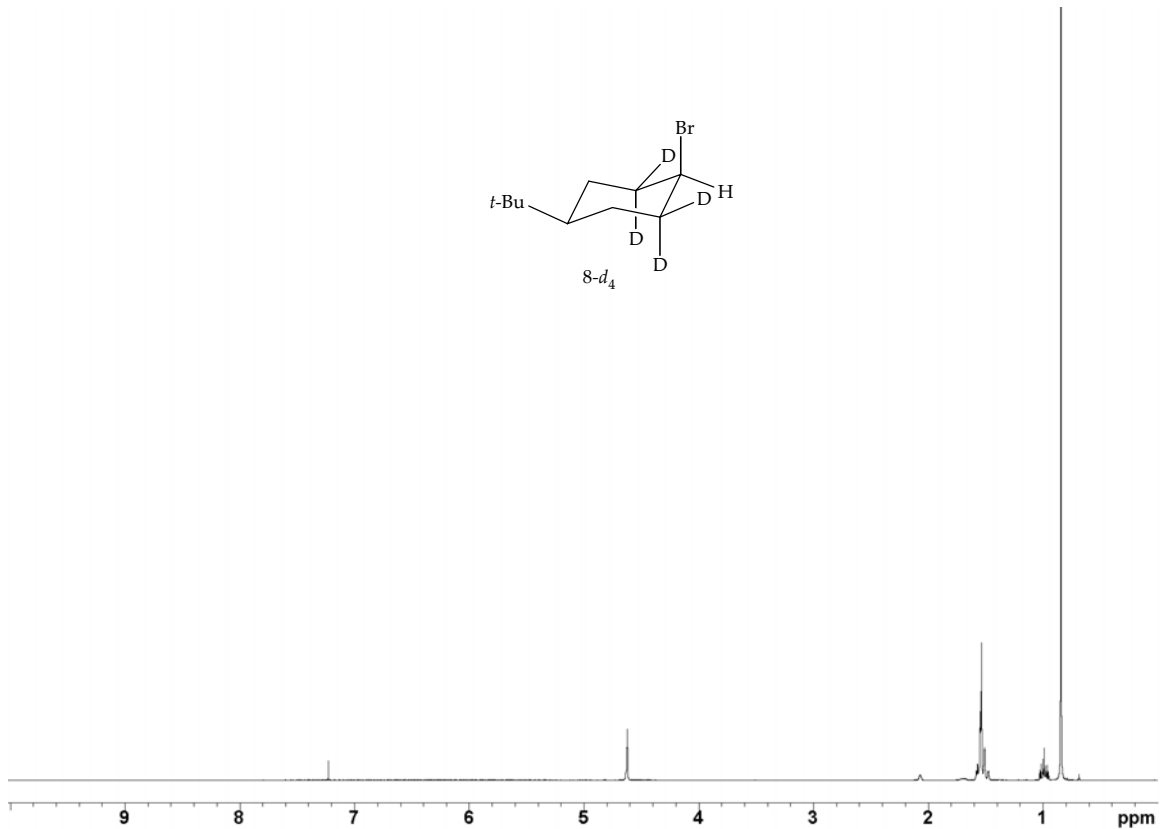
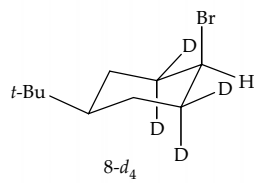
was removed under vacuum. The remaining residue was recrystallized four times from hexane at -96 °C to give *cis*-1-bromo-2,2,5,5-tetradeuterio-4-*tert*-butylcyclohexane (4.5 g, 30% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.67 (1H, s), 1.61 (4H, m), 1.04 (1H, m), 0.88 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 55.0, 47.6, 32.5, 27.4, 21.5; MS *m/z* 143, 127, 85, 57.

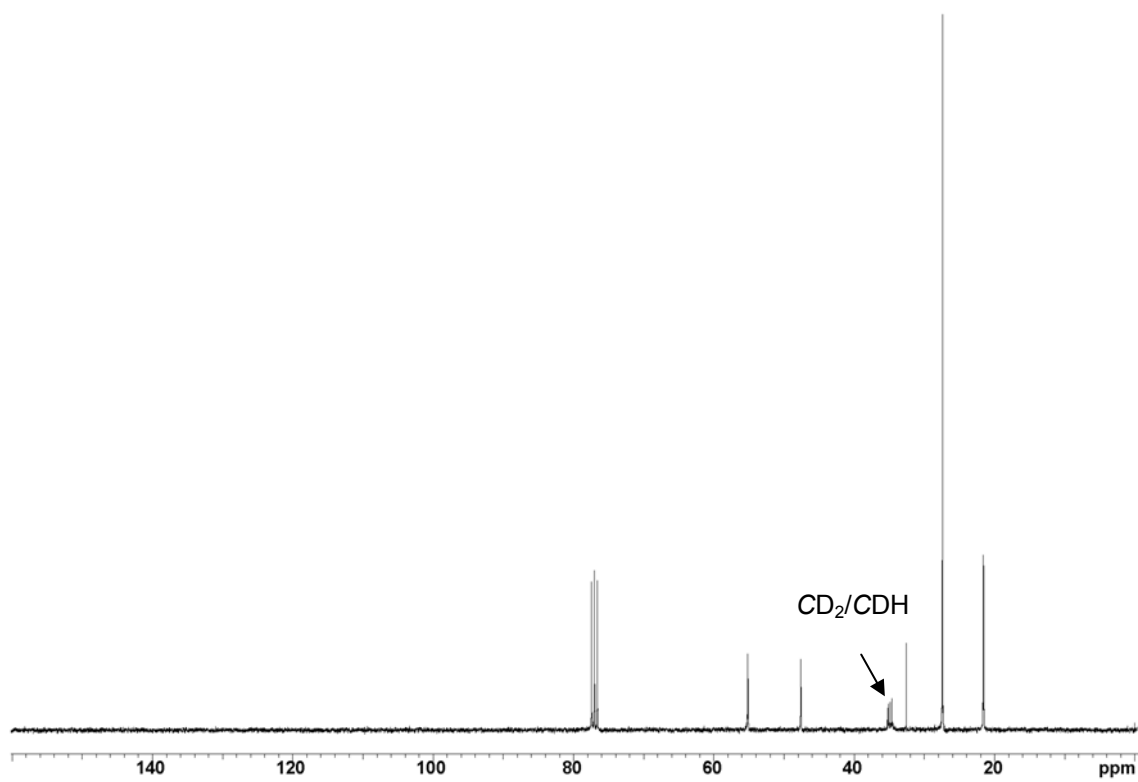
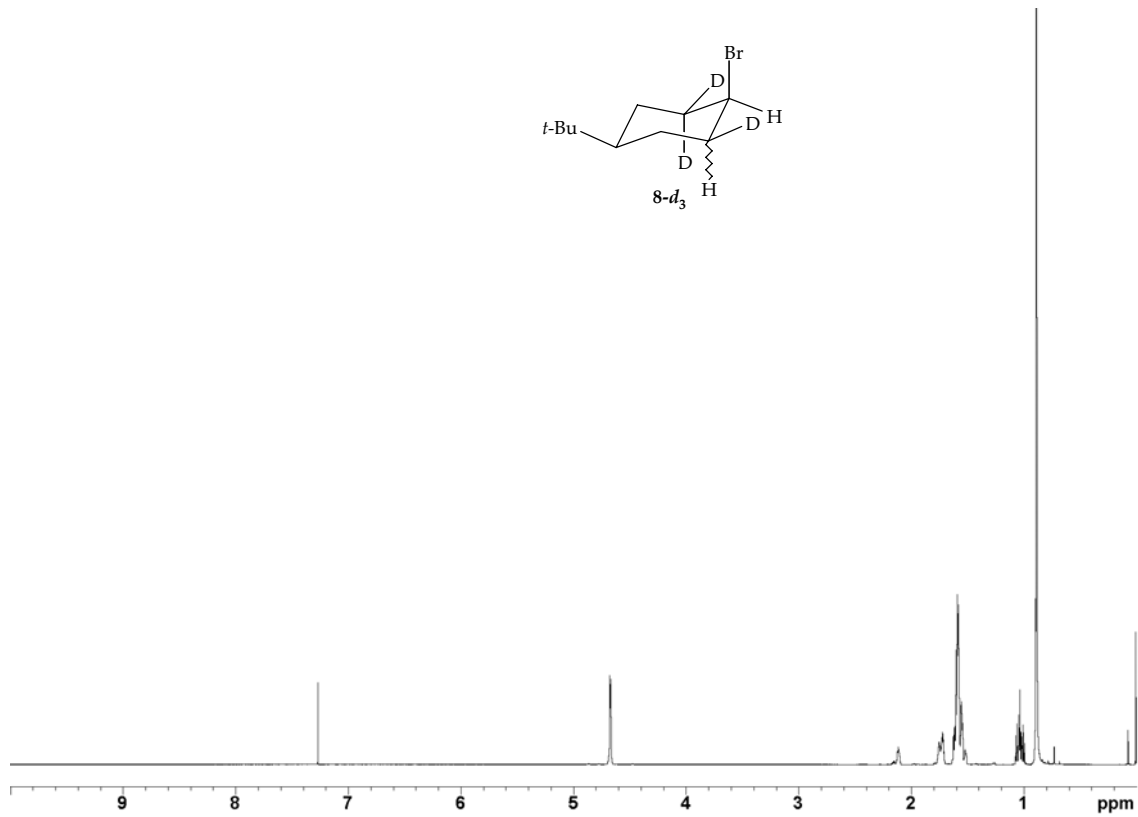
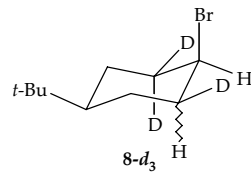


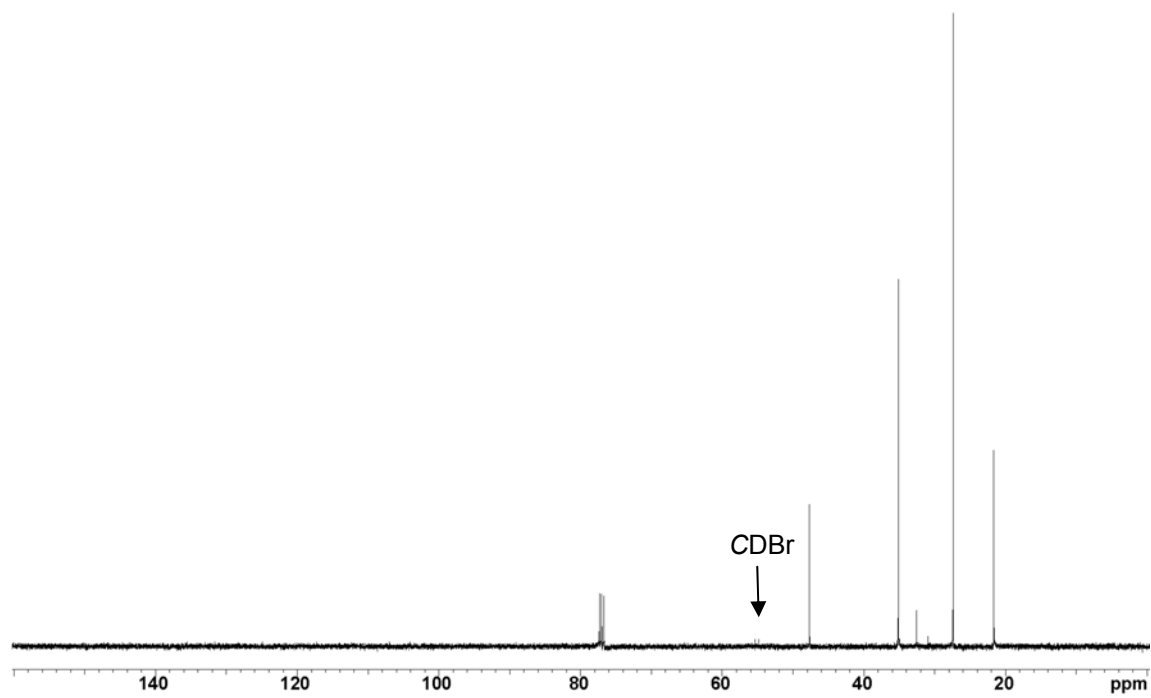
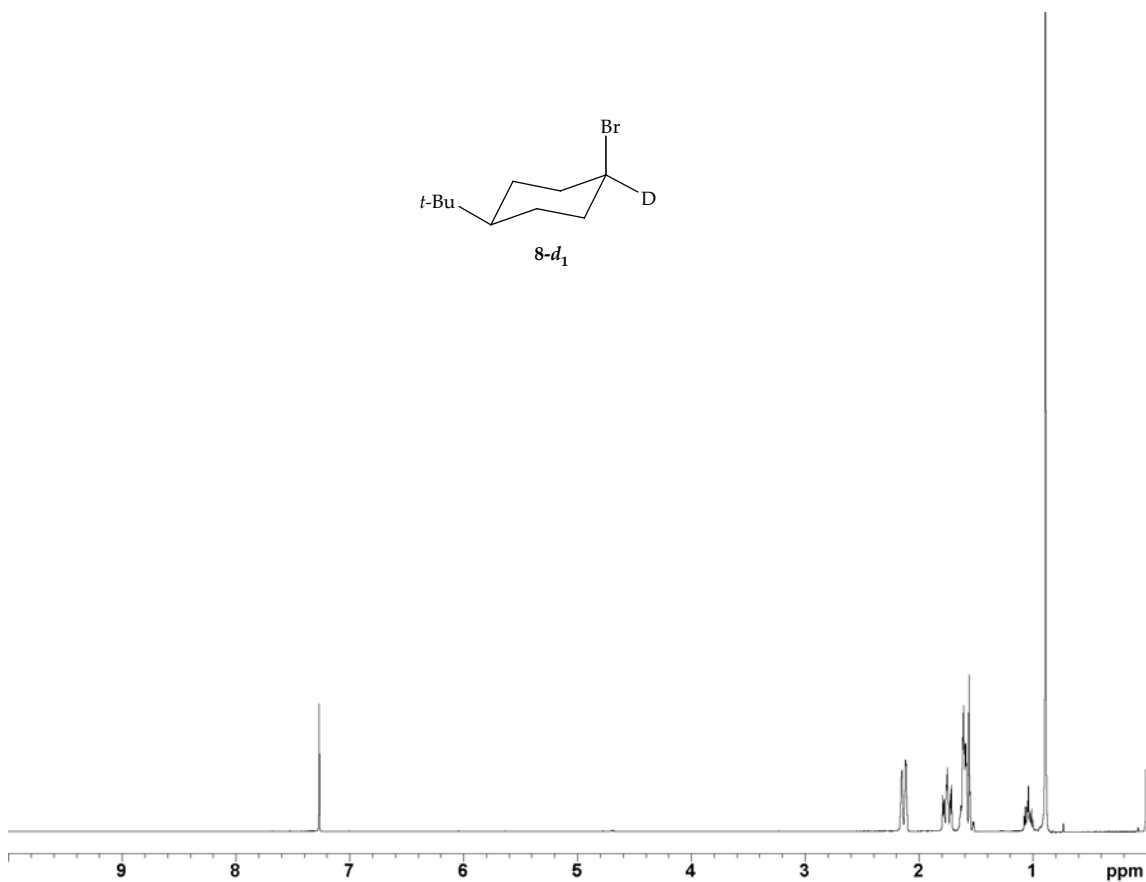
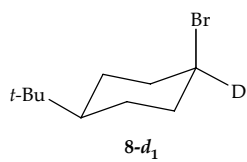
X. Synthesis of *cis*-1-bromo-2,5,5-trideuterio-4-*tert*-butylcyclohexane **8-*d*₃**

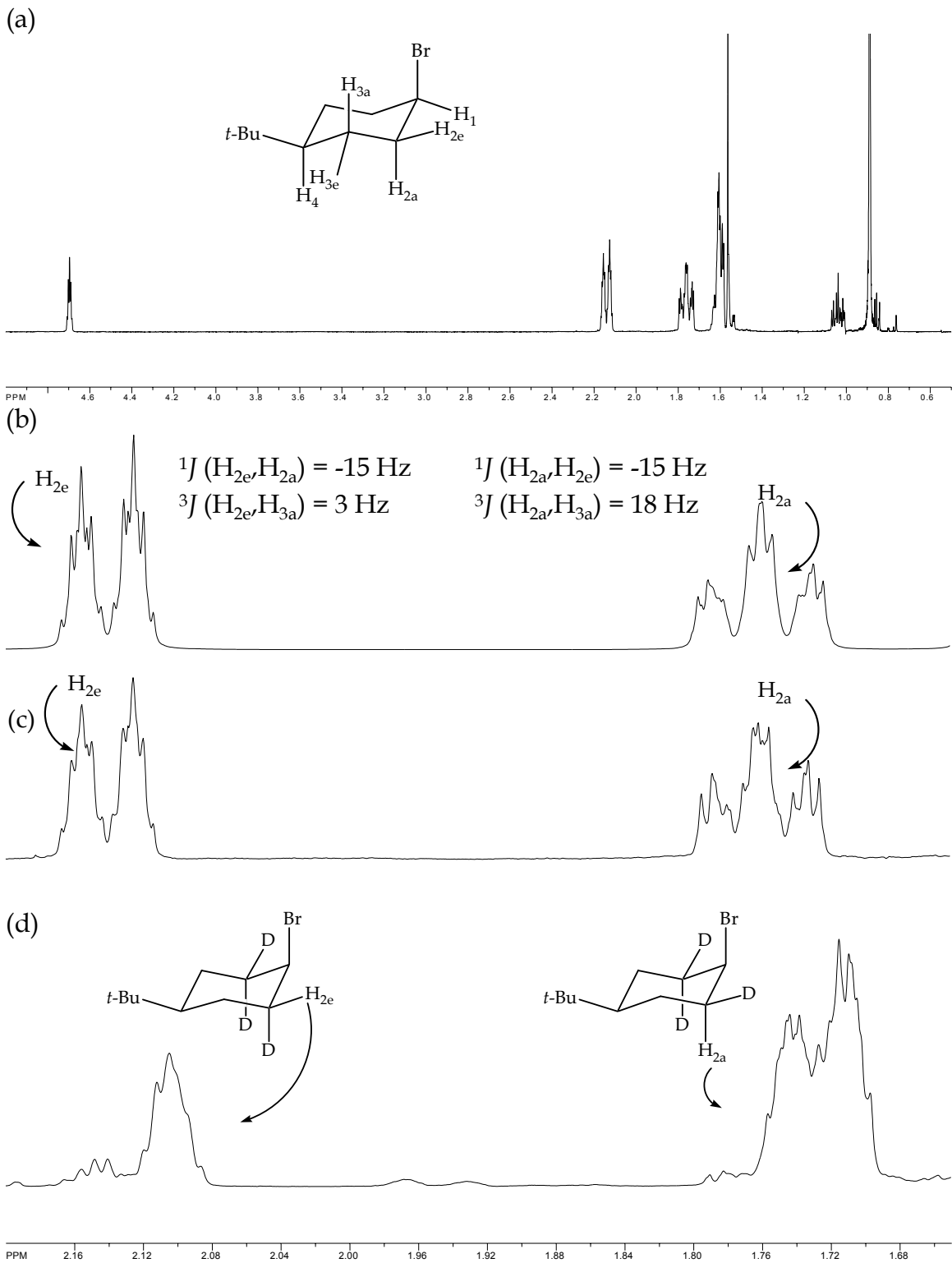
8-*d*₄ (13.0 g, 82.2 mmol) was treated with LDA (9.0 g, 85.0 mmol) in THF (80.0 mL) at -78 °C for 30 min with stirring. A saturated solution of aqueous NH₄Cl (80.0 mL) was added to the mixture. The aqueous layer was extracted with pentane (3 × 20 mL). The combined organic layers were dried with MgSO₄. After the solvent was removed, the product was used directly to prepare 1-bromo-2,5,5-trideuterio-4-*tert*-butylcyclohexanol and *cis* and *trans*-1-bromo-2,5,5-trideuterio-4-*tert*-butylcyclohexane with the same procedures described above. ¹H NMR (400 MHz, CDCl₃) δ 4.66 (1H, d, *J* = 2.8 Hz), 2.11 (1H, m), 1.76 (1H, m), 1.55 (4H, m), 1.03 (1H, m), 0.89 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 47.6, 32.6, 27.4, 21.5; MS *m/z* 142, 126, 84, 69, 57.

XI. ^1H and ^{13}C NMR Spectra:









(a) Experimental ^1H NMR spectrum of **8**; (b) Partial simulated spectrum of **8**; (c) Partial experimental spectrum of **8**; (d) Partial experimental spectrum of **8- d_3** . (H_{2a} and H_{2e} signals of **8- d_3** are shielded due to deuterium substitution).

Chemical shift assignments for *cis*-1-bromo-4-*tert*-butylcyclohexane (**8**) are based on coupling constants determined by spin system simulations (NUMARIT algorithm, Martin, J. S. and Quirt, A. R. *J. Magn. Reson.* **1971**, 5, 318, as implemented in SpinWorks 2.3, Marat, Kirk University of Manitoba). The spectrum of **8** was simulated with the following parameters: chemical shifts (ppm): H₁ 4.70 (1H, m); H_{2e} 2.12 (2H, m); H_{2a} 1.76 (2H, m), H_{3a} and H_{3e} 1.60 (4H, m), H₄ 1.04 (1H, m); coupling constants (Hz): $J(\text{H}_1, \text{H}_{2a})$ 2.80, $J(\text{H}_1, \text{H}_{2e})$ 2.8 Hz; $J(\text{H}_{2a'}, \text{H}_{2e})$ -15.00 Hz; $J(\text{H}_{2a'}, \text{H}_{3a})$ 18.00 Hz; $J(\text{H}_{2a'}, \text{H}_{3e})$ 3.00 Hz, $J(\text{H}_{2e'}, \text{H}_{3a})$ 3.20 Hz; $J(\text{H}_{2e'}, \text{H}_{3e})$ 3.00 Hz, $J(\text{H}_{3a'}, \text{H}_{3e})$ -14.00 Hz; $J(\text{H}_{3a'}, \text{H}_4)$ 11.11 Hz; $J(\text{H}_{3e'}, \text{H}_4)$ 3.20. The simulated spectrum matches the gross features of the experimental spectrum well. However, fine couplings were not accurately reproduced and therefore the above values are considered approximate. The typical coupling constant ranges of cyclohexane derivatives are $^2J_{\text{gem}}$ -11 to -14; $^3J_{\text{ax,ax}}$ 8 to 13; $^3J_{\text{eq,ax}}$ 2 to 6 and $^3J_{\text{eq,eq}}$ 2 to 5 Hz. (Pretsch, E.; Buhlmann, P. and Affolter, C. *Structure Determination of Organic Compounds: Tables of Spectral Data* Springer-Verlag Berlin Heidelberg **2000**, p 176). H_{2a} and H_{2e} could be unambiguously assigned based on having two large couplings ($^2J_{\text{ax,eq}}$; $^3J_{\text{ax,ax}}$) and one large coupling ($^2J_{\text{ax,eq}}$), respectively. Chemical shift assignments of *cis*-1-bromo-2,5,5-trideuterio-4-*tert*-butylcyclohexane **8-d₃** are based on chemical shift similarity to **8**. (δH_1 4.66 (1H, m), H_{2e} 2.11 (1H, m), H_{2a} 1.76 (1H, m).

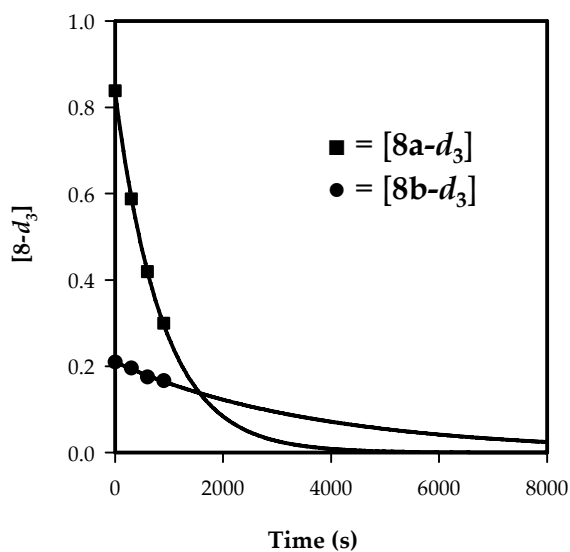
XII. Determination of $k_{\text{obsd}(8\mathbf{a}-d_3)}$ and $k_{\text{obsd}(8\mathbf{b}-d_3)}$

A series of oven-dried, argon-flushed 10.0 mL serum vials (10 per rate constant) fitted with stir bars were charged with a stock solution containing 0.10 M LDA, 0.60 M free HMPA, 10.0 M THF, and hexane. The reaction vials were held under argon at -55.0 ± 0.2 °C. The reactions were initiated by adding a mixture of **8a-d₃** and **8b-d₃** (4:1) to reach a final concentration of 0.004 M containing dodecane as a GC standard. The dehydrobromination was monitored by following the loss of the mixture of **8a-d₃** and **8b-d₃**. The vessels were periodically quenched with H₂O. The quenched aliquots were extracted into hexane and the extracts analyzed using an auto injecting GC fitted with a 60 meter DB-5 column to determine the percent conversion. Each sample was purified by flash chromatography (hexane) and the mixtures were analyzed by ¹H NMR spectroscopy to determine the ratio of **8a-d₃** and **8b-d₃**. The combination of the two analytical methods afforded rate constants for the loss of the **8a-d₃** and **8b-d₃** (See page S21).

XIII. Table of data for Plot XIV^a

Time (s)	[8a-d₃ + 8b-d₃]	8a-d₃ / 8b-d₃ ^b	[8a-d₃]	[8b-d₃]
0	1.05	4.0	0.84	0.21
300	0.78	3.0	0.59	0.20
600	0.59	2.4	0.42	0.17
900	0.47	1.8	0.30	0.16

^aReaction of a 4:1 mixture of **8a-d₃** and **8b-d₃** (0.004 M) with 0.10 M LDA in 0.60 M free HMPA, 10.0 M THF and hexane at -55 °C relative to a dodecane internal standard. ^bRatio was determined by ¹H NMR spectroscopy.

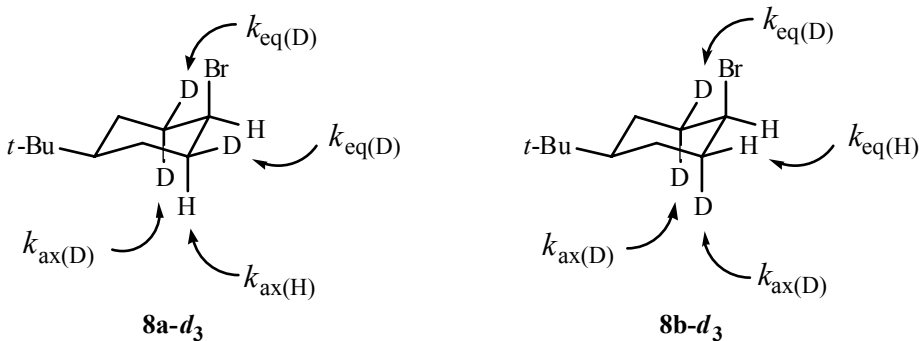


XIV. Plot of [**8a-d₃**] and [**8b-d₃**] vs time fit to the equation $[A]/[A_0] = a^*e^{-k_{\text{obsd}}t}$

where $[A]$ = concentration of **8-d₃** at time, and $[A_0] = [\mathbf{8-d_3}]$ at $t = 0$.

$k_{\text{obsd}(\mathbf{8a-d_3})} = 0.0015 \pm 0.0001 \text{ (s}^{-1}\text{)}$ and $k_{\text{obsd}(\mathbf{8b-d_3})} = 0.00027 \pm 0.00003 \text{ (s}^{-1}\text{)}$

XV. Derivation of an expression for k_{ax}/k_{eq}



$$-d[\mathbf{8a-d}_3]/dt = (k_{ax(H)} + k_{ax(D)} + 2k_{eq(D)}) [\mathbf{8a-d}_3]$$

Because comparison of **8a-d₄** and **8a-d₀** affords $k_H/k_D = 10$, we substitute as follows:

$$-d[\mathbf{8a-d}_3]/dt = (k_{ax(H)} + 0.1k_{ax(H)} + 0.2k_{eq(H)}) [\mathbf{8a-d}_3]$$

$$-d[\mathbf{8a-d}_3]/dt = (1.1k_{ax(H)} + 0.2k_{eq(H)}) [\mathbf{8a-d}_3]$$

Similarly...

$$-d[\mathbf{8b-d}_3]/dt = (k_{eq(H)} + 2k_{ax(D)} + k_{eq(D)}) [\mathbf{8b-d}_3]$$

$$-d[\mathbf{8b-d}_3]/dt = k_{eq(H)} + 0.2k_{ax(H)} + 0.1k_{eq(H)}$$

$$-d[\mathbf{8b-d}_3]/dt = (1.1k_{eq(H)} + 0.2k_{ax(H)}) [\mathbf{8b-d}_3]$$

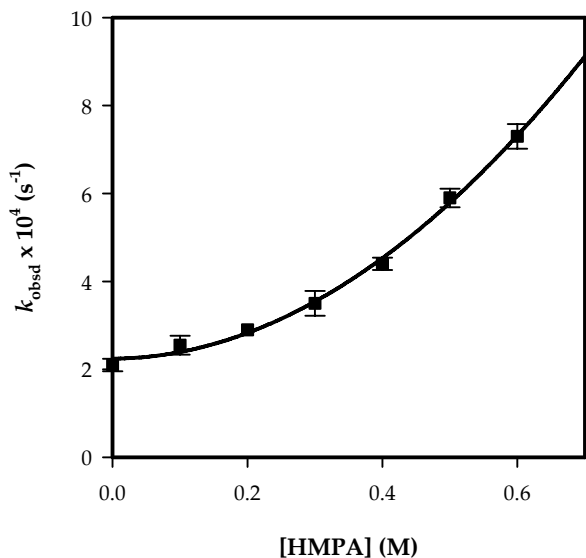
By following the loss of each isomer we can obtain the observed rate constants $k_{\text{obsd}(\mathbf{8a-d}_3)}$ and $k_{\text{obsd}(\mathbf{8b-d}_3)}$ such that

$$k_{\text{obsd}(\mathbf{8a-d}_3)} = 1.1k_{ax(H)} + 0.2k_{eq(H)} \quad (1)$$

$$k_{\text{obsd}(\mathbf{8b-d}_3)} = 1.1k_{eq(H)} + 0.2k_{ax(H)} \quad (2)$$

From Section XIV, $k_{\text{obsd}(\mathbf{8a-d}_3)} = 0.0015 \text{ (s}^{-1}\text{)}$, $k_{\text{obsd}(\mathbf{8b-d}_3)} = 0.00027 \text{ (s}^{-1}\text{)}$

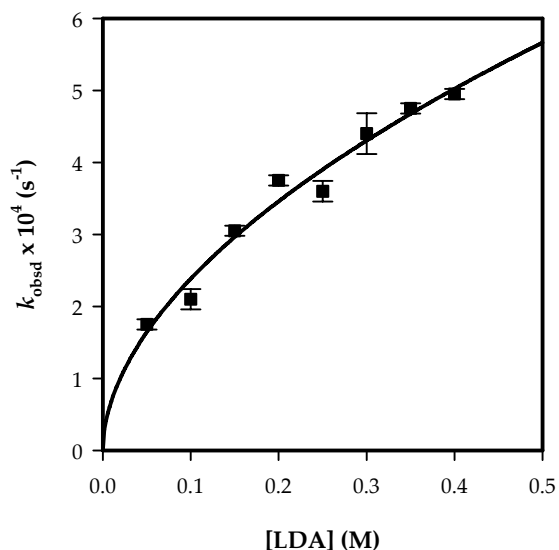
Solving simultaneous eqs. 1 and 2 affords $k_{eq(H)} = 0.000050 \text{ (s}^{-1}\text{)}$ and $k_{ax(H)} = 0.0010 \text{ (s}^{-1}\text{)}$. Therefore, $k_{ax}/k_{eq} = 20$.



XVI. Plot of k_{obsd} vs [HMPA] for the elimination of (\pm)-2-*exo*-bromonorbornane **10** (0.004 M) by 0.10 M LDA in THF (10.0 M)/hexane at 0 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{HMPA}]^n + k'$ ($k = 1.4 \pm 0.1 \times 10^{-3}$, $k' = 2.3 \pm 0.1 \times 10^{-4}$, $n = 2.0 \pm 0.1$).

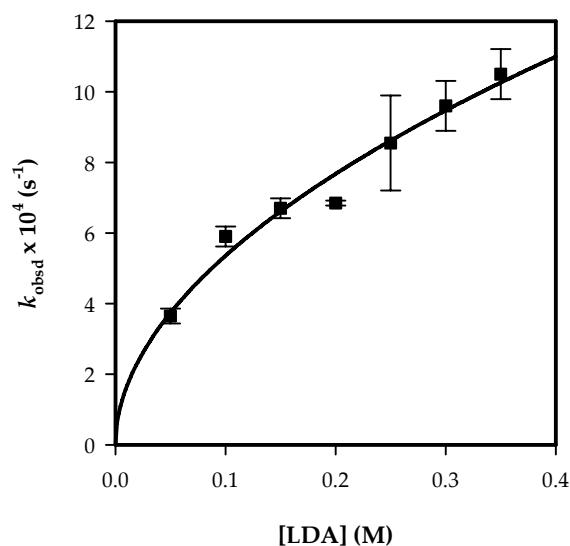
[HMPA] (M) ^a	$k_{\text{obsd1}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd2}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd}} (\text{av}) \times 10^4$ (s ⁻¹)
0.00	2.2 ± 0.1	2.0 ± 0.1	2.1 ± 0.1
0.10	2.7 ± 0.1	2.4 ± 0.2	2.6 ± 0.2
0.20	2.9 ± 0.1	2.9 ± 0.1	2.9 ± 0.0
0.30	3.7 ± 0.2	3.3 ± 0.3	3.5 ± 0.3
0.40	4.3 ± 0.2	4.5 ± 0.1	4.4 ± 0.1
0.50	5.7 ± 0.1	6.0 ± 0.2	5.9 ± 0.2
0.60	7.5 ± 0.2	7.1 ± 0.1	7.3 ± 0.3

^a[HMPA] refers to the concentration of free (uncoordinated) HMPA.



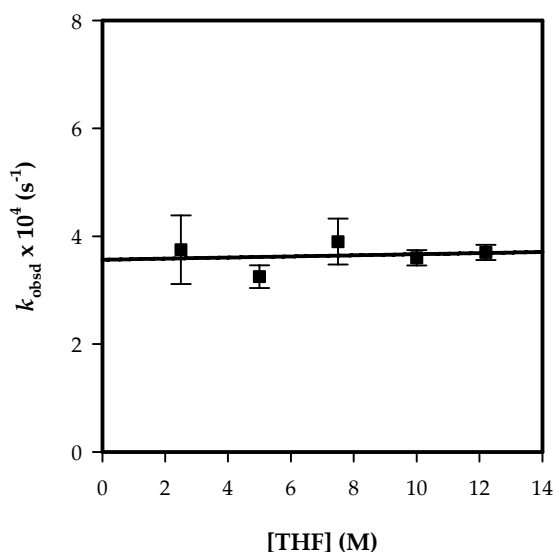
XVII. Plot of k_{obsd} vs [LDA] for the elimination of (\pm)-2-*exo*-bromonorbornane **10** (0.004 M) in 0.10 M free HMPA and THF (10.0 M)/hexane at 0 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LDA}]^n$ ($k = 8.2 \pm 0.5 \times 10^{-4}$, $n = 0.54 \pm 0.04$).

[LDA] (M)	$k_{\text{obsd1}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd2}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd}} (\text{av}) \times 10^4$ (s ⁻¹)
0.05	1.7 ± 0.2	1.8 ± 0.1	1.75 ± 0.07
0.10	2.2 ± 0.1	2.0 ± 0.2	2.1 ± 0.1
0.15	3.1 ± 0.1	3.0 ± 0.2	3.05 ± 0.06
0.20	3.8 ± 0.2	3.7 ± 0.1	3.75 ± 0.07
0.25	3.7 ± 0.1	3.5 ± 0.1	3.6 ± 0.1
0.30	4.6 ± 0.1	4.2 ± 0.2	4.4 ± 0.3
0.35	4.8 ± 0.1	4.7 ± 0.1	4.75 ± 0.08
0.40	4.9 ± 0.1	5.0 ± 0.2	4.95 ± 0.07



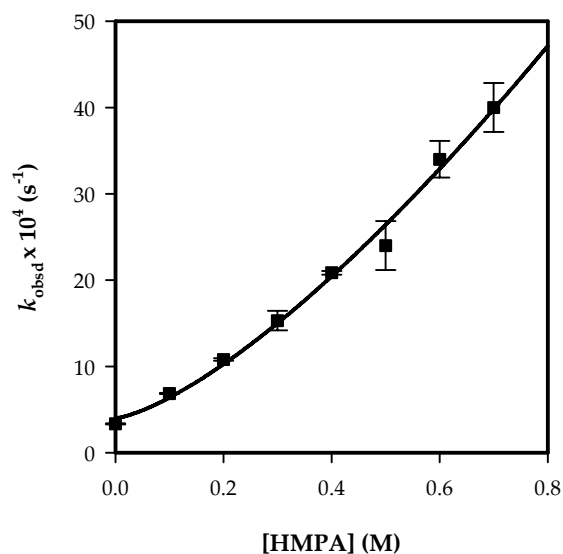
XVIII. Plot of k_{obsd} vs [LDA] for the elimination of (\pm)-2-*exo*-bromonorbornane **10** (0.004 M) in 0.50 M free HMPA and THF (10.0 M)/hexane at 0 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LDA}]^n$ ($k = 1.8 \pm 0.2 \times 10^{-3}$, $n = 0.52 \pm 0.05$)

[LDA] (M)	$k_{\text{obsd1}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd2}} \times 10^4$ (s ⁻¹)	$k_{\text{obsd}} (\text{av}) \times 10^4$ (s ⁻¹)
0.05	3.5 ± 0.1	3.8 ± 0.2	3.6 ± 0.2
0.10	6.1 ± 0.2	5.7 ± 0.1	5.9 ± 0.2
0.15	6.5 ± 0.1	6.9 ± 0.1	6.7 ± 0.2
0.20	6.8 ± 0.2	6.9 ± 0.2	6.85 ± 0.07
0.25	7.6 ± 0.1	9.5 ± 0.1	9 ± 1
0.30	9.2 ± 0.2	10.2 ± 0.2	9.7 ± 0.7
0.35	10.0 ± 0.2	11.0 ± 0.2	10.5 ± 0.7



XIX. Plot of k_{obsd} vs [THF] for the elimination of (\pm)-2-*exo*-bromonorbornane **10** (0.004 M) by 0.10 M LDA in 0.50 M free HMPA/hexane at 0 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}] + k'$ ($k = -5.0 \pm 0.2 \times 10^{-6}$, $k' = 3.5 \pm 0.2 \times 10^{-4}$).

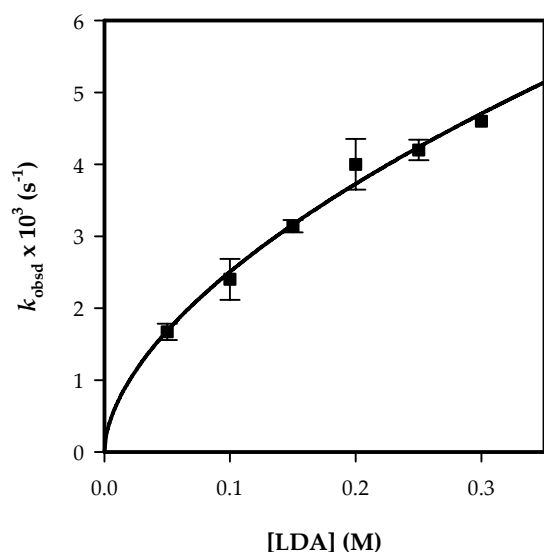
[THF] (M)	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd (av)}} \times 10^4 \text{ (s}^{-1}\text{)}$
2.5	3.3 ± 0.1	4.2 ± 0.1	3.8 ± 0.6
5.0	3.1 ± 0.2	3.4 ± 0.2	3.4 ± 0.2
7.5	4.2 ± 0.1	3.6 ± 0.1	3.6 ± 0.4
10.0	3.7 ± 0.2	3.5 ± 0.3	3.5 ± 0.1
12.2	3.6 ± 0.2	3.8 ± 0.1	3.7 ± 0.1



XX. Plot of k_{obsd} vs [HMPA] for the elimination of 1-bromocyclooctene **12** (0.004 M) by 0.10 M LDA in THF (10.0 M)/hexane at $-10\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{HMPA}]^n + k'$ ($k = 5.8 \pm 0.3 \times 10^{-3}$, $k' = 4.0 \pm 0.1 \times 10^{-4}$, $n = 1.4 \pm 0.1$).

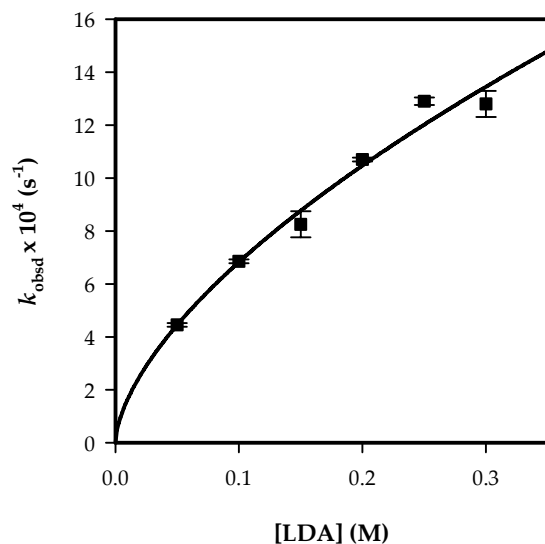
[HMPA] (M) ^a	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^4 \text{ (s}^{-1}\text{)}$
0.00	3.4 ± 0.1	3.3 ± 0.1	3.35 ± 0.07
0.10	6.8 ± 0.1	6.9 ± 0.2	6.85 ± 0.07
0.20	10.9 ± 0.1	10.7 ± 0.1	10.8 ± 0.1
0.30	16.1 ± 0.2	14.5 ± 0.3	15.3 ± 1.1
0.40	20.7 ± 0.2	21.0 ± 0.1	20.9 ± 0.2
0.50	26.0 ± 0.1	22.0 ± 0.2	24 ± 3
0.60	35.0 ± 0.2	32.0 ± 0.3	34 ± 2
0.70	42.0 ± 0.2	38.0 ± 0.2	40 ± 3

^a[HMPA] refers to the concentration of free (uncoordinated) HMPA.



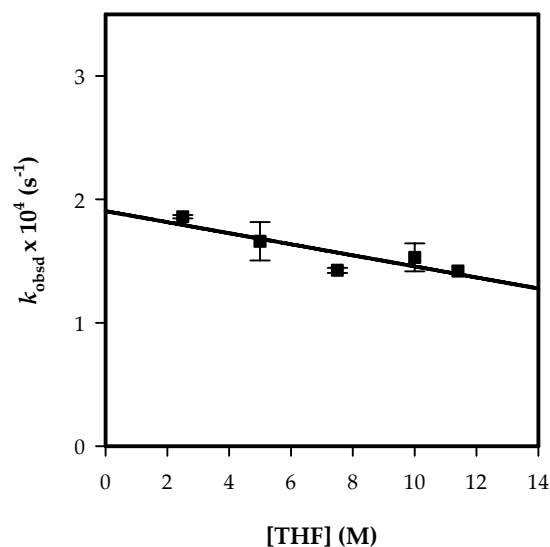
XXI. Plot of k_{obsd} vs [LDA] for the elimination of 1-bromocyclooctene **12** (0.004 M) in 0.50 M free HMPA/THF (10.0 M)/hexane at $-10\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LDA}]^n$ ($k = 9.4 \pm 0.5 \times 10^{-3}$, $n = 0.57 \pm 0.04$)

[LDA] (M)	$k_{\text{obsd1}} \times 10^3 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^3 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd (av)}} \times 10^3 \text{ (s}^{-1}\text{)}$
0.05	1.75 ± 0.01	1.59 ± 0.01	1.7 ± 0.1
0.10	2.6 ± 0.1	2.2 ± 0.2	2.4 ± 0.3
0.15	3.2 ± 0.1	3.08 ± 0.02	3.14 ± 0.08
0.20	4.2 ± 0.4	3.7 ± 0.1	4.0 ± 0.4
0.25	4.1 ± 0.1	4.3 ± 0.1	4.2 ± 0.1
0.30	4.6 ± 0.1	4.6 ± 0.2	4.6 ± 0.0



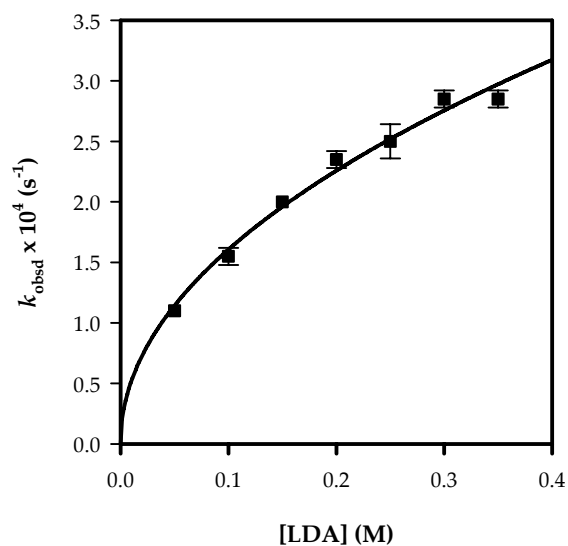
XXII. Plot of k_{obsd} vs [LDA] for the elimination of 1-bromocyclooctene **12** (0.004 M) in 0.10 M free HMPA/THF (10.0 M)/hexane at $-10\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LDA}]^n$ ($k = 2.7 \pm 0.2 \times 10^{-3}$, $n = 0.61 \pm 0.04$)

[LDA] (M)	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^4 \text{ (s}^{-1}\text{)}$
0.05	4.5 ± 0.1	4.4 ± 0.3	4.45 ± 0.07
0.10	6.8 ± 0.2	6.9 ± 0.1	6.85 ± 0.07
0.15	7.9 ± 0.1	8.6 ± 0.1	8.3 ± 0.5
0.20	10.7 ± 0.2	10.6 ± 0.2	10.7 ± 0.07
0.25	13.0 ± 0.1	12.8 ± 0.1	12.9 ± 0.1
0.30	13.1 ± 0.2	12.4 ± 0.2	12.8 ± 0.5



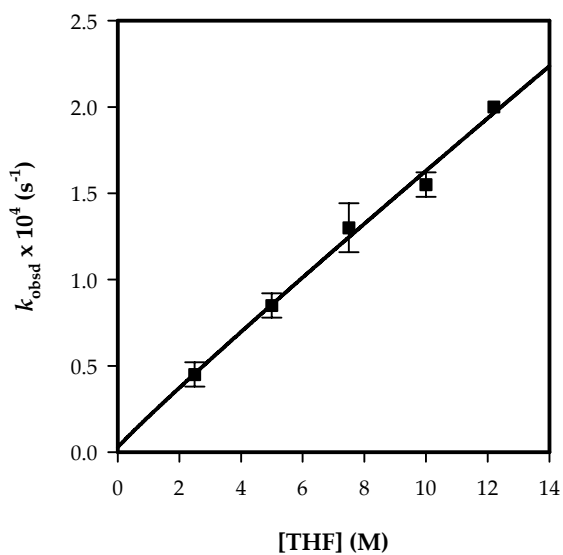
XXIII. Plot of k_{obsd} vs [THF] for the elimination of 1-bromocyclooctene **12** (0.004 M) by 0.10 M LDA in 0.30 M free HMPA/hexane at -10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}] + k'$ ($k = -4.5 \pm 0.1 \times 10^{-6}$, $k' = 1.9 \pm 0.1 \times 10^{-5}$).

[THF] (M)	$k_{\text{obsd}1} \times 10^4$ (s ⁻¹)	$k_{\text{obsd}2} \times 10^4$ (s ⁻¹)	$k_{\text{obsd}} (\text{av}) \times 10^4$ (s ⁻¹)
2.50	1.87 ± 0.01	1.85 ± 0.06	1.86 ± 0.01
5.00	1.77 ± 0.02	1.55 ± 0.02	1.7 ± 0.2
7.50	1.44 ± 0.01	1.41 ± 0.01	1.43 ± 0.02
10.0	1.61 ± 0.02	1.45 ± 0.03	1.5 ± 0.1
11.6	1.42 ± 0.02	1.42 ± 0.03	1.42 ± 0.00



XXIV. Plot of k_{obsd} vs $[\text{LDA}]$ for the elimination of 1-bromocyclooctene **12** (0.004 M) in THF (10.0 M)/hexane at 0 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LDA}]^n$ ($k = 5.0 \pm 0.2 \times 10^{-4}$, $n = 0.50 \pm 0.03$)

$[\text{LDA}] \text{ (M)}$	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^4 \text{ (s}^{-1}\text{)}$
0.05	1.1 ± 0.1	1.1 ± 0.4	1.1 ± 0.0
0.10	1.5 ± 0.2	1.6 ± 0.2	1.55 ± 0.07
0.15	2.0 ± 0.4	2.0 ± 0.1	2.0 ± 0.0
0.20	2.3 ± 0.2	2.4 ± 0.2	2.35 ± 0.07
0.25	2.4 ± 0.1	2.6 ± 0.1	2.5 ± 0.1
0.30	2.9 ± 0.2	2.8 ± 0.1	2.85 ± 0.07
0.35	2.8 ± 0.2	2.9 ± 0.4	2.85 ± 0.07



XXV. Plot of k_{obsd} vs [THF] for the elimination of 1-bromocyclooctene **12** (0.004 M) by 0.10 M LDA in hexane at 0 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}]^n + k'$ ($k = 1.8 \pm 0.2 \times 10^{-5}$, $k' = 3.6 \pm 0.2 \times 10^{-5}$, $n = 0.93 \pm 0.05$).

[THF] (M)	$k_{\text{obsd1}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (av)} \times 10^4 \text{ (s}^{-1}\text{)}$
2.5	0.50 ± 0.01	0.40 ± 0.01	0.45 ± 0.07
5.0	0.90 ± 0.02	0.80 ± 0.02	0.85 ± 0.07
7.5	1.4 ± 0.1	1.2 ± 0.1	1.3 ± 0.1
10.0	1.5 ± 0.2	1.6 ± 0.1	1.55 ± 0.07
12.2	2.0 ± 0.2	2.0 ± 0.1	2.0 ± 0.0

XXVI. Bibliography of Triple Ions

Triple ions--lithium 'ate' complexes of general structure $X_2Li-/+Li-$ were first mentioned by Fuoss more than 70 years ago.^{ref 1} They appear prominently in the literature of inorganic salts (electrolytes).^{ref 2} The first mention of triple ions in the context of organolithium chemistry appears to have been by Wittig in 1951.^{ref 3} Many carbanion-based triple ions have been observed and discussed subsequently.^{ref 4,5} Of particular interest are triple ions derived from N-lithiated species^{ref 4,5} and those based on the $+Li(HMPA)_4$ counterion.^{ref 6}

1. Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1933**, *55*, 2387.
2. *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. 1 and 2. Saar, D.; Petrucci, S. J. *Phys. Chem.* **1986**, *90*, 3326. Hojo, M.; Ueda, T.; Nishimura, M.; Hamada, H.; Matsui, M.; Umetani, S. *J. Phys. Chem. B* **1999**, *103*, 8965. Hojo, M.; Ueda, T.; Chen, Z.; Nishimura, M. *J. Electroanal. Chem.* **1999**, *468*, 110. Lascaud, S.; Perrier, M.; Armand, M.; Prud'homme, J.; Kapfer, B.; Vallee, A.; Gauthier, M. *Electrochim. Acta* **1998**, *43*, 1407. Chen, Z.; Hojo, M. *J. Phys. Chem. B* **1997**, *101*, 10896. Hojo, M.; Hasegawa, H.; Miyauchi, Y.; Moriyama, H.; Yoneda, H.; Arisawa, S. *Electrochim. Acta* **1994**, *39*, 629. Hojo, M.; Miyauchi, Y.; Nakatani, I.; Mizobuchi, T.; Imai, Y. *Chem. Lett.* **1990**, 1035. Hojo, M.; Fujime, C.; Yoneda, H. *Chem. Lett.* **1993**, 37. Miyauchi, Y.; Hojo, M.; Moriyama, H.; Imai, Y. *J. Chem. Soc., Faraday Trans.* **1992**, 3175. Fenton, D. E.; Nave, C.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2188. Beronius, P.; Lindbäck, T. *Acta Chem. Scand.* **1978**, *A32*, 423. Beronius, P.; Lindbäck, T. *Acta Chem. Scand.* **1979**, *A33*, 397. Cachet, H.; Cyrot, A.; Fekir, M.; Lestrade, J.-C. *J. Phys. Chem.* **1979**, *83*, 2419. Nishikawa, S.; Morinaga, S.; Yoshio, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3627. Vinogradova, L. V.; Zgonnik, V. N.; Nikolaev, N. I.; Tsvetanov, K. B. *Eur. Polym. J.* **1979**, *15*, 545. Tsvetanov, Ch. B.; Dotcheva, D. T. *J.*

Polym. Sci., Part A, Polym. Chem. **1986**, 24, 2253. Strohmeier, V. W.; Landsfeld, H.; Gernert, F. Z. *Elektrochem.* **1962**, 66, 823. Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. J. *Phys. Chem.* **1965**, 69, 612. Gill, J. B. *Pure Appl. Chem.* **1987**, 59, 1127. Huyskens, P. L.; Verheyden, H.; Van Lierde, P. *J. Mol. Liq.* **1998**, 78, 151.

3. Wittig, G.; Meyer, F. J.; Lange, G. *Justus Liebigs Ann. Chem.* **1951**, 571, 167. Wittig, G. *Angew. Chem.* **1958**, 70, 65.

4. Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Sivik, M. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1994**, 116, 6466. Paquette, L. A.; Bauer, W.; Sivik, M. R.; Buehl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, 112, 8776. Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, 103, 5657. Tombul, M.; Errington, R. J.; Coxall, R. A.; Clegg, W. *Acta Crystallogr., Sect. C* **2003**, C59, m231. Verheyden, H.; Van Lierde, P.; Szwarc, M.; Litvinenko, G.; Van Beylen, M. *V. J. Polym. Sci., Part A: Polym. Chem.* **2002**, 40, 2148. Gareyev, R.; Ciula, J. C.; Streitwieser, A. *J. Org. Chem.* **1996**, 61, 4589. Arnett, E. M.; Maroldo, S. G.; Schriver, G. W.; Schilling, S. L.; Troughton, E. B. *J. Am. Chem. Soc.* **1985**, 107, 2091. Bauer, W.; O'Doherty, G. A.; Schleyer, P. v. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991**, 113, 7093. Cambillau, C.; Bram, G.; Corset, J.; Riche, C. *Nouv. J. Chim.* **1979**, 3, 9. Cambillau, C.; Ourevitch, M. *J. Chem. Soc., Chem. Commun.* **1981**, 996. Raban, M.; Noe, E. A.; Yamamoto, G. *J. Am. Chem. Soc.* **1977**, 99, 6527. Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* **1980**, 45, 3299. Teixidor, F.; Llobet, A.; Casabo, J.; Solans, X.; Font-Altava, M.; Aguiló, M. *Inorg. Chem.* **1985**, 24, 2315. Eaborn, C.; Hitchcock, J. D.; Smith, P. B.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827. Viteva, L.; Stefanovskii, Y.; Tsvetanov, C.; Gorrichon, L. *J. Phys. Org. Chem.* **1990**, 3, 205. Hertkorn, N.; Köhler, F. H. *Z. Naturforsch. B: Chem. Sci.* **1990**, 45, 848. Bhattacharyya, D. N.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1964**, 86, 5024. Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, 12, 2126. Gornitzka, H.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 693. Eiermann, M.;

Hafner, K. *J. Am. Chem. Soc.* **1992**, *114*, 135. Khan, I. M.; Hogen-Esch, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2553. Dotcheva, D.; Tsvetanov, C. B.; Lochmann, L. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 3005. Kocienski, P.; Barber, C. *Pure Appl. Chem.* **1990**, *62*, 1933. Corset, J. *Pure Appl. Chem.* **1986**, *58*, 1133. Arnold, J.; Dawson, D. Y.; Hoffman, C. G. *J. Am. Chem. Soc.* **1993**, *115*, 2707. Cioslowski, J.; Piskorz, P.; Schimeczek, M.; Boche, G. *J. Am. Chem. Soc.* **1998**, *120*, 2612. Dohmeier, C.; Baum, E.; Ecker, A.; Koppe, R.; Schnockel, H. *Organometallics* **1996**, *15*, 4702. Ashe, A. J., III; Kampf, J. W.; Muller, C.; Schneider, M. *Organometallics* **1996**, *15*, 387. Sivik, M. R.; Bauer, W.; Schleyer, P. v. R.; Paquette, L. A. *Organometallics* **1996**, *15*, 5202. Böhler, B.; Hüls, D.; Günther, H. *Tetrahedron Lett.* **1996**, *37*, 8719. Böhler, B.; Günther, H. *Tetrahedron Lett.* **1996**, *37*, 8723. Schroeder, F. A.; Weber, H. P. *Acta Crystallogr. B*, **1975**, *31*, 1745. Adler, H. J.; Lochmann, L.; Dotcheva, D. T.; Tsvetanov, C. B. *Makromol. Chem.* **1986**, *187*, 1253. Schade, P.; Schaefer, T.; Muellen, K. *Chem. Ber.* **1991**, *124*, 2833. Wiberg, K. B.; Sklenak, S.; Bailey, W. F. *Organometallics* **2001**, *20*, 771.

5. Hosmane, N. S.; Yang, J.; Zhang, H.; Maguire, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 5150. Eaborn, C.; Lu, Z. R.; Hitchcock, P. B.; Smith, J. D. *Organometallics* **1996**, *15*, 1651. Jackman, L. M.; Rakiewicz, E. F. *J. Am. Chem. Soc.* **1991**, *113*, 1202. Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524. Jackman, L. M.; Scarmoutzos, L. M.; Smith, B. D.; Williard, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 6058. Gutierrez-Garcia, V. M.; Reyes-Rangel, G.; Munoz-Muniz, O.; Juaristi, E. *Helv. Chim. Acta* **2002**, *85*, 4189. Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Stamper, J. G.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 969. Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976. Pauer, F.; Rocha, J.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1477. Shirley, D. A.; Hendrix, J. P. *J. Organomet. Chem.* **1968**, *11*, 217. Baker, D. R.; Clegg, W.; Horsburgh, L.; Mulvey, R. E. *Organometallics* **1994**, *13*, 4170. Gornitzka, H.; Stalke, D. *Organometallics* **1994**, *13*, 4398. Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 3546.

Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751. Romesberg, F. E.; Bernstein, M. P.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475. Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 9198. Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 2452. Leung, W.-P.; Cheng, H.; Hou, H. L.; Yang, Q.-C.; Wang, Q.-G.; Mak, T. C. W. *Organometallics* **2000**, *19*, 5431.

6. Reich, H. J.; Green, D. P.; Medina, M. A.; Goldenberg, W. J.; Gudmundsson, B. Ö.; Dykstra, R. R.; Philips, N. H. *J. Am. Chem. Soc.* **1998**, *120*, 7201. Reich, H. J.; Sikorski, W. H.; Gudmundsson, B. Ö.; Dykstra, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4035. Reich, H. J.; Holladay, J. A.; Mason, J. D.; Sikorski, W. H. *J. Am. Chem. Soc.* **1995**, *117*, 12137.