J. Am. Chem. Soc. **1988**, *110*, 5109-5112

Unusual Stability of an Alkyllithium Dimer. Preparation, Properties, and Decomposition Mechanism of $(t\text{-BuLi}\cdot 2OEt_2)_2$

Tim F. Bates, Matthew T. Clarke, and Ruthanne D. Thomas*

Contribution from the Center for Organometallic Research and Education, Department of Chemistry, North Texas State University, Denton, Texas 76203. *Received November 23, 1987*

Abstract: Variable-temperature ^{13}C and ^{6}Li NMR spectroscopy were used to study the interaction and reaction of ethyl ether with *tert*-butyllithium-^{6}*Li* in cyclopentane. Addition of ethyl ether to hydrocarbon solutions of *tert*-butyllithium produces a dynamic, temperature-dependent equilibrium between uncoordinated tetramers and tetracoordinated dimers with $\Delta H = -36 \pm 3$ kcal/mol and $\Delta S = -155 \pm 15$ eu. Surprisingly, solutions with oxygen to lithium ratios of 2 or less show no signs of decomposition after several hours at −80 °C, whereas solutions with a ratio greater than 2 begin to decompose immediately. This is explained in terms of the reaction of the tetracoordinated dimer with only free ether as the rate-determining step in the reaction. This may have implications for synthetic procedures normally carried out with *tert*-butyllithium in diethyl ether at low temperature.

Many reactions of tetrameric alkyllithium in ether solvents presumably involve deaggregated species (i.e. dimers or monomers) as the reactive intermediates.[1] The dimer of *n*-BuLi has recently been shown to be present in THF solutions,[2,3] while *t*-BuLi is monomeric in THF and dimeric in ethyl ether.[4] A more detailed understanding of the nature and reactivity of these smaller coordinated aggregates would be highly desirable, but their increased reactivity results in a significantly decreased lifetime. Other researchers have circumvented this problem by devising intramolecularly coordinated alkyllithium compounds that are stable in hydrocarbon solvent[5] or by using very rapid spectroscopic techniques.[3] We now report that tetracoordinated *t*-BuLi dimer $(t\text{-BuLi}\cdot 2OEt_2)_2$ can be prepared and is stable below −35 °C in hydrocarbon solvent when less than a stoichiometric amount of ether is used. We have taken advantage of this improved stability to study the tetramer–dimer equilibrium as well as to study the mechanism of reaction of *t*-BuLi with ethyl ether.

Results and Discussion

The addition of ethyl ether to a hydrocarbon solution of *tert*-butyllithium results in a dynamic, temperature-dependent mixture of uncoordinated tetramers and tetracoordinated dimers (eq 1).

$$(t\text{-BuLi})_4 + 8OEt_2 \rightleftarrows 2[t\text{-BuLi}\cdot 2OEt_2]_2 \qquad (1)$$

The dimer is characterized by a five-line multiplet for the α-carbon at 12.8 ppm with ^{6}Li–^{13}C coupling of 7.8 Hz (Figure 1). Such a five-line multiplet, with relative peak intensities of 1:2:3:2:1, is exactly that expected for a nucleus coupled to two ^{6}Li nuclei ($I = 1$).[2] The observed coupling of 7.8 Hz is consistent with the ^{7}Li–^{13}C coupling of 20 Hz observed earlier for *tert*-butyllithium dimers[4] as well as ^{6}Li–^{13}C coupling for other alkyllithium dimers in coordinating solvents.[6] The ^{6}Li resonance for the dimer is a single sharp peak 0.25 ppm downfield of the tetramer peak.

Table I. Concentration of *t*-BuLi Tetramer, $(t\text{-BuLi})_4$, and Coordinated Dimer, $(t\text{-BuLi}\cdot 2OEt_2)_2$, as a Function of Temperature and Et_2O Concentration

temp, °C	[dimer], mol/L	[tetramer], mol/L	$[Et_2O]_{free}$,[a] mol/L	K_{eq}[b]
	$[RLi]_{init} = 1.08$ F, $[Et_2O] = 0.866$ M			
−90.8	0.204	0.168	0.050	6.34×10^9
−80.4	0.170	0.185	0.186	1.09×10^5
−69.7	0.143	0.198	0.294	1.85×10^3
−57.5	0.103	0.218	0.454	27.0
−46.3	0.0803	0.230	0.545	3.60
−35.4	0.0621	0.239	0.618	0.758
	$[RLi]_{init} = 0.99$ F, $[Et_2O] = 0.91$ M			
−90.8	0.21	0.14	0.07	5.5×10^8
−80.4	0.20	0.15	0.11	1.24×10^7
−69.7	0.18	0.16	0.19	1.19×10^5
−57.5	0.14	0.18	0.35	4.84×10^2
−46.3	0.092	0.20	0.542	5.68
	$[RLi]_{init} = 1.00$ F, $[Et_2O] = 1.24$ M			
−90.8	0.304	0.098	0.033	6.71×10^{11}
−80.4	0.289	0.105	0.084	2.89×10^{10}
−69.7	0.242	0.129	0.272	3.71×10^4
−57.5	0.197	0.152	0.432	2.35×10^2
−46.3	0.156	0.172	0.616	9.20
−35.4	0.123	0.189	0.748	0.950

[a] Concentration of uncoordinated ethyl ether calculated from $[OEt_2]_{initial} - 4[(t\text{-BuLi}\cdot 2OEt_2)_2]$. [b] $K_{eq} = [\text{dimer}]^2/[Et_2O]_{free}{}^8[\text{tetramer}]$.

The *tert*-butyllithium tetramer is assumed to be uncoordinated by ethyl ether even in the presence of excess ether since the ^{13}C chemical shifts, the observed ^{6}Li–^{13}C coupling of 5.4 Hz, and the temperature-dependent changes in the ^{6}Li–^{13}C coupling (i.e. fluxional exchange) are identical with those for *tert*-butyllithium in cyclopentane without ethyl ether.[7] Apparently steric hindrance by the *tert*-butyl groups is sufficient to prevent coordination of the lithium atoms in the tetramer.

Evaluation of Thermodynamic Parameters. The relative concentrations of the dimer and tetramer were determined from integration of the ^{6}Li spectra. A typical set of ^{6}Li spectra as a function of temperature is shown in Figure 2. These spectra were completely reversible over the temperature range studied. As was typical of all of the solutions observed in this study (O:Li = 0.8–16), the equilibrium in eq 1 is shifted to the right at −90 °C. (The spectrum at −90 °C shown in Figure 2 contains a significant amount of tetramer since ethyl ether is present as the limiting reagent.) At −20 °C the same solutions consist almost entirely as uncoordinated tetramers (upfield ^{6}Li peak).

---

(1) (a) Wardell, J. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, pp 43–120. (b) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974. Although, see: (c) Brown, T. L. *J. Organomet. Chem.* **1966**, *5*, 191.

(2) Seebach, D.; Hassig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308.

(3) (a) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 1805. (b) McGarrity, J. F.; Ogie, C. A.; Brich, Z.; Loosli, H. *J. Am. Chem. Soc.* **1985**, *107*, 1810.

(4) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371–2379.

(5) (a) Vos, M.; de Kanter, F. J. J.; Schakel, M.; van Eikema Hommes, N. J. R.; Klumpp, G. W. *J. Am. Chem. Soc.* **1987**, *109*, 2187–2188. (b) Geurink, P. J. A.; Klumpp, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 538–539.

(6) (a) PhLi, 8 Hz: Fraenkel, G., Hsu, H., Su, B. M. In *Lithium, Current Applications in Science, Medicine and Technology*; Bach, O., Ed.; Wiley: New York, 1985, p 273. (b) *n*-BuLi, 7.8 Hz; ref 2. (c) PhC≡CLi. 8.2 Hz: Hassig, R.; Seebach, D. *Helv. Chim. Acta.* **1983**, *66*, 2269–2273.

(7) Thomas, R. D.; Clarke, M. T.; Jensen, R. M. *Organometallics* **1986**, *5*, 1851–1857.

0002-7863/88/1510-5109$01.50/0

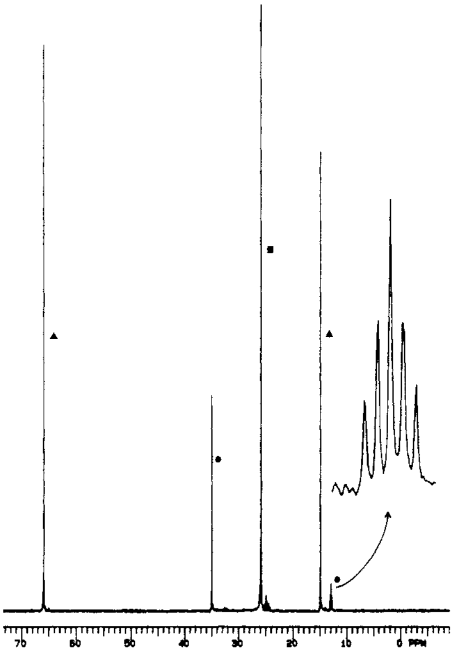


Figure 1. 75-MHz ^{13}C NMR spectrum of $(t\text{-}Bu^6Li{\cdot}2OEt_2)_2$ in cyclopentane/diethyl ether at −80 °C. [*t*-BuLi] = 1.0 F, $[Et_2O]$ = 2.8 M. (■), cyclopentane; (●), dimer; (▲), ether.

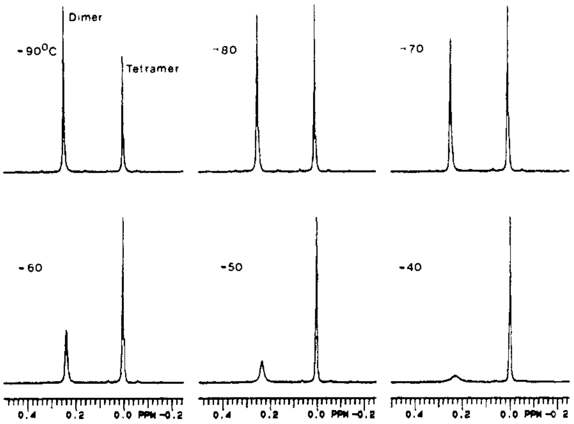


Figure 2. 44-MHz variable-temperature ^6Li NMR spectra of $t\text{-}Bu^6Li$/diethyl ether in cyclopentane. [*t*-BuLi] = 1.0 F, $[Et_2O]$ = 1.24 M.

The equilibrium constant, $K_{eq} = [\text{dimer}]^2/[\text{free ether}]^8[\text{tetramer}]$, was determined as a function of temperature by integration of the ^6Li spectra. The concentrations of each species in solution and the derived equilibrium constants are listed in Table I. Since no direct measurement of free vs coordinated ether was possible due to rapid exchange of ether molecules on the NMR time scale, the concentration of free ether was taken to be $[OEt_2]_{\text{initial}} - 4[\text{dimer}]$.

A plot of ln (K_{eq}) vs 1000/*T* (Figure 3) results in $\Delta H = -36 \pm 3$ kcal/mol and $\Delta S = -155 \pm 15$ eu. The large negative ΔS is reasonable considering the large reduction in entropy associated with going from nine reactant molecules to only two product molecules and is in line with the smaller ΔS of −47 eu observed for $(n\text{-}BuLi{\cdot}THF)_4 + 4THF \rightarrow 2(n\text{-}BuLi{\cdot}2THF)_2$.[8]

The enthalpy change can be broken into two contributions, an endothermic term, $\Delta H_{4\rightarrow 2}$, due to the dissociation of the tetramer to dimers, and an exothermic term, $8\Delta H_{\text{solv}}$, due to coordination or solvation of the eight ether molecules to the lithium dimers:

$$\Delta H = \Delta H_{4\rightarrow 2} + 8\Delta H_{\text{solv}} \qquad (2)$$

We earlier found ΔH^{*} for the fluxional exchange of *tert*-butyllithium in cyclopentane to be 25 kcal/mol.[7] The rate-determining step for this exchange process is apparently either dissociation of the tetramer to dimers or dissociation of the tetrahedral tetramer to an eight-membered ring.[9] If we take 25 kcal/mol as a lower limit to the dissociation of tetramer to dimer, $\Delta H_{4\rightarrow 2}$, then ΔH_{solv} is −7.6 kcal/mol. Although calorimetry data have been used to measure the heat of solvation of alkyllithium compounds,[10] the effects of dissociation and solvation have been separated in relatively few studies.[3,8] The ΔH_{solv} of −7.6 kcal/mol is somewhat smaller than the −10 kcal/mol reported for *n*-BuLi in THF[3] and is consistent with the greater steric crowding and the weaker base in this study.

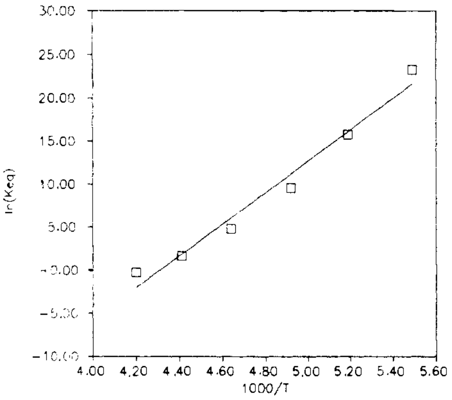


Figure 3. Plot of ln K_{eq} vs 1000/*T*, where $K_{eq} = [\text{dimer}]^2/[\text{free ether}]^8[\text{tetramer}]$. Each point, except −35 °C, is the average of one determination from each of the three samples listed in Table I.

Table II. Initial Rate of Disappearance of Tetracoordinated *tert*-Butyllithium Dimer in Cyclopentane/Ethyl Ether at −80 °C

$[\text{ether}]_{\text{initial}}$, mol/L	[dimer],[a] mol/L	$[\text{ether}]_{\text{free}}$,[b] mol/L	−d[dimer]/d*t*,[c] mol/L s
3.69	0.310	2.45	1.7×10^{-5}
5.97	0.187	5.22	2.2×10^{-5}
6.13	0.301	4.93	4.0×10^{-5}
5.10	0.388	3.54	3.0×10^{-5}

[a] Concentration of $(t\text{-}BuLi{\cdot}2OEt_2)_2$ calculated as 0.5 $[RLi]_{\text{total}}$. [b] Concentration of uncoordinated ethyl ether calculated from $[OEt_2]_{\text{initial}} - 4[(t\text{-}BuLi{\cdot}2OEt_2)_2]$. [c] Estimated initial rate of disappearance of dimer.

Reaction of $(t\text{-}BuLi{\cdot}2OEt_2)_2$ with OEt_2. In the course of the above studies, we observed that solutions with a deficient or stoichiometric (O:Li = 2:1) amount of diethyl ether showed no signs of decomposition at −80 °C after several hours. Even when heated to 40 °C for 35 min, a mixture of ethyl ether and *tert*-butyllithium (O:Li = 1:1.8) showed only 11% reduction in the size of the dimer peak after recooling to −60 °C. On the other hand, solutions with an O:Li ratio greater than 2 began to decompose rapidly even at −80 °C. This suggested that only free ether reacts with *tert*-butyllithium dimer. Although the reaction of alkyllithiums with ethers has been extensively studied,[11] the kinetically active alkyllithium species is not known. To study the mechanism of reaction of *t*-BuLi and ethyl ether, the rate of disappearance of the dimer was determined for solutions with different O:Li ratios at −80 °C.

The rate of disappearance of the dimer was monitored as a function of time by ^6Li NMR for samples with O:Li ratios ranging from 2.4 to 16. The rate of reaction was clearly dependent on the concentrations of both free ether and dimer, but attempts to

---

(8) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848–1862. The ΔS value of −47 eu was calculated by converting K'_{eq} to K_{eq} byl using [THF] = 13.57 mol/L. See Appendix E of ref 8.

(9) A third proposed mechanism, rotation of three alkyl groups relative to the lithium core, has been found to be unlikely based on ^6Li T_1 NMR studies of *tert*-butyllithium. Thomas, R. D.; Ellington, D. H., unpublished results.

(10) See, for example: (a) Quirk, R. P.; Kester, D. E. *J. Organomet. Chem.* **1977**, *127*, 111. (b) Kminek, I.; Kaspar, M.; Trekoval, J. *Collect. Czech. Chem. Commun.* **1981**, *45*, 1124. (c) Kminek, I.; Kaspar, M.; Trekoval, J. *Collect. Czech. Chem. Commun.* **1981**, *45*, 1132.

(11) (a) Holm, T. *Acta Chem. Scand., Ser B* **1978**, 162–166. (b) Maercker, A.; Demuth, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 75–76 and references therein.

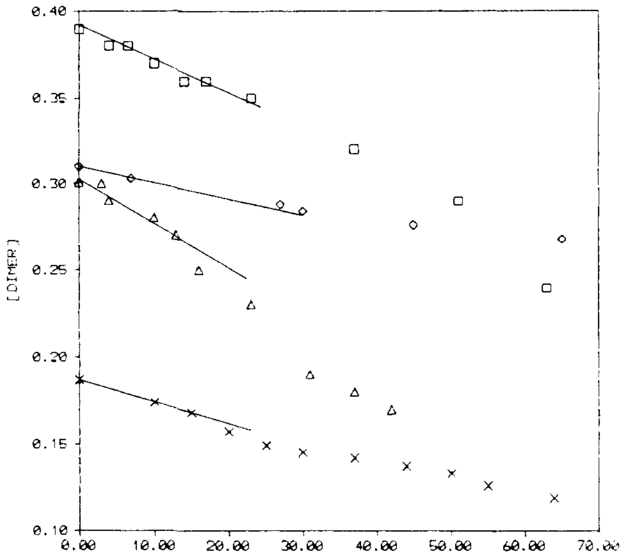


Figure 4. Concentration of $(t\text{-Bu}^6\text{Li}\cdot 2\text{OEt}_2)_2$ vs time (minutes) at −80 °C was determined by integration of the ^{6}Li spectra. (□), $[\text{dimer}]_{\text{init}}$ = 0.388 M, [free ether] = 3.54 M; (◇), $[\text{dimer}]_{\text{init}}$ = 0.310 M, [free ether] = 2.45 M; (△), $[\text{dimer}]_{\text{init}}$ = 0.301 M, [free ether] = 4.93 M; (X), $[\text{dimer}]_{\text{init}}$ = 0.187 M, [free ether] = 5.22 M.

define the rate of reaction in some simple manner were complicated at low O:Li ratios by relatively slow formation of the dimer from the tetramer. For samples with O:Li ratios of >4, dimers are formed sufficiently rapidly that the decay of dimer is proceeding smoothly by the time the first NMR spectrum is recorded. Plots of the concentration of dimer vs time for a series of these solutions are shown in Figure 4.

Initial rates of reaction were estimated from these plots and are listed in Table II. A plot of ln (rate/[free ether]) vs ln [dimer] yields a straight line with a slope of 1.0 ± 0.3, indicating that the reaction is first order in dimer. Likewise, a plot of ln (rate/[dimer] vs ln [free ether] yields a straight line with a slope of 1.1 ± 0.2, indicting the reaction is also first order in free ether. The rate expression for the reaction of dimer with ethyl ether is then

$$\text{rate} = k[\text{dimer}][\text{free ether}] \tag{3}$$

where k is 2.3×10^{-5} L mol^{-1} s^{-1}. Since the reaction is first order in dimer, then the tetracoordinated dimer is the reactive species. (Reaction of ether with monomer requires $^1/_2$ order in dimer, while reaction of ether with tetramer requires second order in dimer.)

Reaction of t-BuLi with ethyl ether also occurs at higher temperatures, even at low O:Li ratios. This may indicate reaction of ether with kinetically more accessible lithium in fluxional *tert*-butyllithium tetramers. However, this reaction is still relatively slow.

The initial products from the reaction of t-BuLi with diethyl ether are assumed to be isobutane, lithium ethoxide, and ethylene.[12] Ethylene was never observed. However 2,2-dimethylbutane was observed by GC–MS following hydrolysis of the samples, indicating the formation of (3,3-dimethylbutyl)lithium from t-BuLi and ethylene, as reported earlier.[12b]

Free lithium ethoxide was also not observed. However, the mixed aggregate $t\text{-Bu}_3(\text{OEt})\text{Li}_4$ was assigned on the basis of the similarity of the ^{6}Li and ^{13}C NMR spectra to that observed for $t\text{-Bu}_3(t\text{-BuO})\text{Li}_4$.[7] The 3:1 mixed tetramer exhibits two signals in the ^{6}Li NMR spectrum in a ratio of 3:1 at +0.35 and −0.03 ppm (relative to t-BuLi tetramer) at −80 °C. The α-carbon of the *tert*-butyl groups is a seven-line multiplet in the ^{13}C spectra below −25 °C (Figure 5) and a nine-line multiplet above 25 °C. This behavior is indicative of the change from a static to a intramolecularly fluxional tetramer, similar to that observed earlier for $(t\text{-BuLi})_4$ and $t\text{-Bu}_3(t\text{-BuO})\text{Li}_4$.[7] Additional peaks at between −0.2 and −0.9 ppm in the ^{6}Li NMR spectra have been tentatively identified as $t\text{-BuLi}_n(\text{OEt})_{6-n}\text{Li}_6$. This assignment is based on the similarity of the ^{6}Li chemical shifts with those of mixed hexameric *tert*-butoxide aggregates $(t\text{-BuO})_n(t\text{-Bu})_{6-n}\text{Li}_6$ ($n \geq 2$).[13]

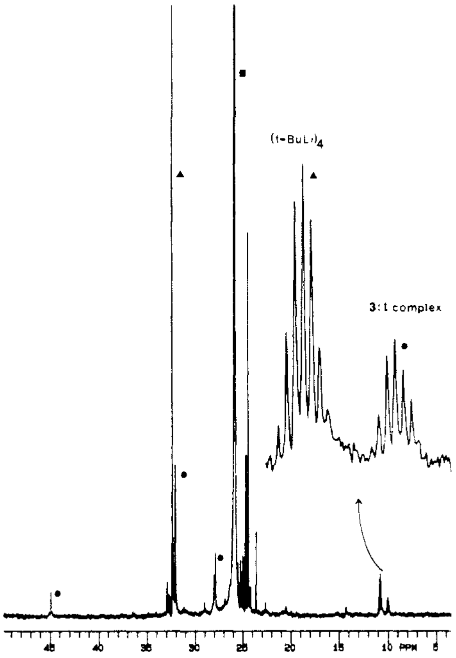


Figure 5. 75-MHz ^{13}C NMR spectrum at −60 °C of $t\text{-Bu}^6\text{Li}/^6\text{LiOEt}$ mixture formed from reaction of 0.25 equiv of diethyl ether with t-BuLi in cyclopentane for 1 week at room temperature. (■), cyclopentane; (▲), $(t\text{-BuLi})_4$; (●), $(t\text{-BuLi})_3(\text{OEt})\text{Li}_4$.

The data outlined above show that the coordinated t-BuLi dimer, $(t\text{-BuLi}\cdot 2\text{OEt}_2)_2$, is the reactive organometallic species in the reaction of t-BuLi with ethyl ether in predominantly hydrocarbon solvent. More importantly, the coordinated dimer is stable in the absence of additional ethyl ether. It may be possible to exploit this stability synthetically for conditions where t-BuLi is normally consumed by the solvent at rates competitive with its reaction with an organic substrate. In these cases, use of t-BuLi in a mixture of cyclopentane with ≤2 equiv of ethyl ether may produce reactive t-BuLi without consumption of t-BuLi by the solvent. Studies are currently in progress in our laboratory to determine if the coordinated dimer is the kinetically reactive species in the reaction of t-BuLi with other Lewis bases, as well as to more completely characterize the organometallic species present in ether-rich solvents.

Experimental Section

All laboratory manipulations involving the synthesis and sample preparation of air-sensitive compounds were performed in a high vacuum system or in an argon-filled drybox with recirculating atmosphere through an oxygen scavenger. Cyclopentane and diethyl ether were dried over LiAlH_4 and degassed on the vacuum line. Syringes, NMR tubes, and volumetric glassware were dried and then kept under vacuum overnight in the drybox port prior to use.

Preparation of t-Bu^{6}Li. Halide-free t-Bu^{6}Li was prepared from di-*tert*-butyl)mercury and 95.5% isotopically enriched ^{6}Li metal (U.S. Services) as described earlier.[7] All t-BuLi was sublimed prior to use.

Preparation of NMR Samples. In a typical experiment, 0.063 g (1.0 mmol) of t-Bu^{6}Li was weighed in the drybox and dissolved in 1.0 mL of cyclopentane (8% cyclopentane-d_{10}, Wilmad; 92% cyclopentane, 99.9%, Wiley Organics). The solution was transferred to a 5-mm NMR tube and capped with a septum. Outside the drybox, the septum was wrapped with parafilm and the NMR tube was cooled in a dry ice/acetone bath. The sample was then placed in the precooled probe of the NMR spectrometer, and a control spectrum was run to determine the purity of the sample prior to addition of ether. Only samples with ≤2.0% $(t\text{-Bu})_3(t\text{-BuO})\text{Li}_4$, as determined by integration of the ^{6}Li spectrum,[7] were used. Diethyl ether was added by gas-tight syringe, and the sample was mixed

---

[12] (a) Bartlett, P. D.; Friedman, S.; Stiles, M. *J. Am. Chem. Soc.* **1953**, *75*, 1771–1772. (b) Mulvaney, J. E.; Gandlund, Z. G. *J. Org. Chem.* **1965**, *30*, 917–920.

[13] Thomas, R. D.; Clarke, M. T., unpublished results.

well, with cooling, immediately before placed back in the NMR probe.

The sample used to obtain the spectrum in Figure 5 was made in a similar manner (1.00 mmol of *t*-Bu^{6}Li, 0.25 mmol of diethyl ether, diluted with cyclopentane to 1.00 mL) except it was degassed and sealed under vacuum. The sample was then held at room temperature for over a week. The solution remained clear and free of precipitate, in contrast to samples with higher oxygen to lithium ratios, which contained white precipitate upon reaction.

NMR Parameters and Conditions. All NMR spectra were obtained on a Varian VXR-300 at 75 and 44 MHz for ^{13}C and ^{6}Li, respectively. Typical conditions for ^{13}C NMR were 18° flip angle, 2.857-s repetition rate, 17 500-Hz spectral width, 32K transform, 128–1024 transients, Waltz proton decoupling. All chemical shifts were set relative to TMS by setting the resonance for protonated cyclopentane to 25.8 ppm.

Typical conditions for ^{6}Li spectra were one transient, 90° flip angle, 300-Hz spectral width, and 32K transform. Spectra were run with gated proton decoupling, such that there was proton decoupling but no NOE. All ^{6}Li chemical shifts are relative to $(t\text{-Bu}^6\text{Li})_4$ at 0.00 ppm.

The temperature within the NMR probe was determined from the difference in the ^{1}H chemical shifts of methanol peaks by using the algorithm supplied by the NMR manufacturer. Decoupling power was kept to a minimum to avoid heating of the sample.

Kinetic Measurements. The change in percent dimer as a function of time was determined from integration of the ^{6}Li NMR spectra. Only single transient spectra with no NOE were used for quantitative measurements. The initial rate of disappearance of dimer was estimated from the concentration of dimer vs time curve at the beginning of the reaction. Rates were determined from only the first 10% of the reaction, or less, to avoid problems with competing reactions such as reaction of the dimer with mixed *t*-BuLi/LiOEt aggregates. Rates were only measured for samples with sufficient excess of ethyl ether (O:Li ≥ 4) to assure rapid formation of the coordinated dimer.

Hydrolysis and GC–MS of Samples. Several of the samples used for NMR analysis were also analyzed by GC–MS. In those cases, the NMR tube was opened and a saturated solution of NH_4Cl was added. Mass spectra of the organic portion was obtained with a Hewlett-Packard 5970A GC–MS and data station.

Acknowledgment. We thank the Robert A. Welch Foundation and North Texas State University Organized Research Funds for financial support of this work.

Registry No. $(t\text{-Bu}^6\text{Li})_4$, 36833-94-0; $[t\text{-Bu}^6\text{Li}\cdot 2\text{OEt}_2]_2$, 114719-00-5; OEt_2, 60-29-7; t-Bu^{6}Li, 103258-93-1.

Homoaromatic Delocalization in the Transition State for Norcaradiene Formation

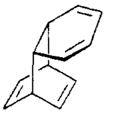
Achim Bertsch,[†] Wolfram Grimme,*,[†] Gerd Reinhardt,[†] Hermann Rose,[†] and Philip M. Warner*,[‡]

Contribution from the Institut für Organische Chemie der Universität Köln, Greinstrasse 4, D-5000 Köln 41, West Germany, and the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received November 4, 1987. Revised Manuscript Received February 29, 1988*

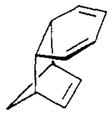
Abstract: The kinetics for the extrusion of benzene from norcaradiene adducts **11** and **12** have been measured. The high **11**/**12** rate ratio, 8.9 × 10^3, was shown to be due to homoaromatic interactions in the cycloreversion transition state emanating from **11**. This conclusion was reached after studying the benzene extrusion kinetics for several model compounds, including **20**. The syntheses of the requisite compounds are fully described.

For some time we have been studying the relationship between structure and reactivity for [4 + 2] cycloreversions involving the extrusion of benzene. We have shown that, in the case of **1** and its higher condensed analogues, the rate of cycloreversion is a linear function of the developing aromatic resonance energy.[1] We have used this finding as a strong argument for concert in these cycloreversions.

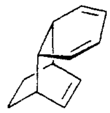
As illustrated by the benzene adducts **2**[2] and **3**,[3] strain energy effects appear to have a large effect on the rate of cycloreversion. At 164 °C, the more strained **2** reacts 1.9 × 10^5 faster than **3**.



1



2



3

We now report a very large difference in the cycloreversion reactivities of diastereomers **11** and **12** and further experiments aimed at differentiating between steric (strain) and electronic effects in these reactions.

The synthesis of **11** and **12** proceeded from homobarrelene, **4**. Diels–Alder reaction of **4** with dimethoxytetrachlorocyclopentadiene at 100 °C gave adducts **5a** and **6a** in a 5:2 ratio. The endo,endo configurations of **5a** and **6a** were demonstrated via their photocyclizations to the caged derivatives **7a** and **8a**. The mixture of **5a** and **6a** was dechlorinated with Na/NH$_3$, following which ketals **5b** and **6b** were separated and purified by crystallization and chromatography. Ketones **9** and **10**, obtained via hydrolysis of **5b** and **6b** in 80% acetic acid, were converted to **11** and **12** via flash pyrolysis.

As detailed in the Experimental Section, the distinction between **5a** and **6a** was made on the basis of the upfield NMR shift experienced by the cyclopropyl methylene of **5a**, compared to that of **6a**. The two stereoisomers required vastly different temperatures for cycloreversion. Thus while **11** yielded benzene at 65 °C, the same process for **12** required 165 °C. The kinetic parameters for the cycloreversion of **11** between 77 and 95 °C were measured by monitoring the concentration of evolved cycloheptatriene (at 303 nm). The first-order rate constants (see Table I) were sub-

---

[†] Institut für Organische Chemie der Universität Köln.

[‡] Department of Chemistry, Iowa State University.

(1) Bertsch, A.; Grimme, W.; Reinhardt, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 377.

(2) Rye, A. R.; Wege, D. *Aust. J. Chem.* **1974**, *27*, 1943.

(3) Grimme, W.; Reinhardt, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 617.

0002-7863/88/1510-5112$01.50/0