Structure and Reactivity of Lithium Amides. $^6$Li, $^{13}$C, and $^{15}$N NMR Spectroscopic Studies and Colligative Measurements of Lithium Diphenylamide and Lithium Diphenylamide–Lithium Bromide Complex Solvated by Tetrahydrofuran

Jeffrey S. DePue and David B. Collum*

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301. Received January 11, 1988

Abstract: $^6$Li, $^{13}$C, and $^{15}$N NMR spectroscopic studies of lithium diphenylamide in THF/hydrocarbon solutions (THF \(=\) tetrahydrofuran) detected two different species. $^6$Li and $^{15}$N NMR spectroscopic studies of $[^6$Li,$^{15}$N]lithium diphenylamide showed the species observed at low THF concentrations to be a cyclic oligomer. Structural analogies provided strong support for a dimer while colligative measurements at 0 °C indicated the dimer to be di- or trisolvated. On the basis of the observed mass action effects, the species appearing at intermediate THF concentrations is assigned as a contact or solvent-separated ion-paired monomer. Lithium diphenylamide forms a 1:1 adduct with lithium bromide at low THF concentrations. A combination of $^6$Li-$^{15}$N double labeling studies and colligative measurements supports a trisolvated cyclic mixed dimer structure. Although detailed spectroscopic studies at elevated THF concentrations were precluded by high solubility, the similarity of the $^6$Li chemical shifts of lithium diphenylamide in the presence and absence of lithium bromide provide indirect evidence that the mixed dimer undergoes a THF concentration dependent dissociation to the monomeric amide and free lithium bromide.

The importance of organolithium reagents in organic chemistry has increased since the turn of the century.\(^{(1)}\) We suspect, for example, that well over 95% of the contemporary natural product syntheses use one or more lithium-containing reagents. Within this very broad class of synthetically reactive reagents, the reactive lithium amide bases and related N-lithiated species have played pivotal roles in the development and refinement of carbon–carbon bond forming reactions.

We will describe in two parts studies of lithium diphenylamide. The first part details $^6$Li, $^{13}$C, and $^{15}$N NMR spectroscopic studies and colligative measurements that provide aggregation state and solvation state data. We will provide evidence that (1) at reduced THF concentrations lithium diphenylamide exists as a di- or trisolvated dimer (1a or 1b) in the absence of LiBr and a trisolvated mixed dimer (2a) in the presence of LiBr and (2) aggregates 1 and 2a dissociate to a common monomeric or ion-paired amide 3 of ill-defined solvation state at elevated THF concentrations.\(^{(4)}\)


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Structure and Reactivity of Lithium Amides

A summary of the results unadorned with experimental details

vent-free Ph₂NLi

solvent-free form, references to LiBr in solution are not intended

an analytically pure, hydrocarbon-insoluble white solid (eq 1).

of [6Li]Ph₂NLi at varying THF concentrations and ambient probe

0.05-0.19 ppm relative to a 0.30 M 6LiCl/methanol external

simplicity is consistent with virtually any structural form exhibiting

either maximum possible symmetry or undergoing rapid chemical

abilities, we turned to 6Li-15N double labeling techniques.

Cyclic oligomeric, and ion triplet forms of lithium amides.

spectroscopy provides the number of lithium atoms connected

approximately settled upon the preparation based on benzene diazonium

spectrum recorded at

-90 °C displays a 1:2:3:2:1 pentuplet (JLi-N

constant are fully consistent with Li-N-Li connectivity.

(Figure 1). The singlet of Ph₂NLi at 0.16 ppm (0.15 M THF,

0.015 M THF; (B) 6Li NMR spectrum: 0.015 M, 0.25 M THF; (C) 15N

NMR spectrum: 0.05 M, 0.15 M THF. The chemical shifts are refer-

identical samples containing external standards.

N-Li connectivities, lithium diphenylamide can be assigned

as a cyclic oligomer with alternating nitrogen and lithium nuclei.

Higher cyclic oligomers, predicted by MNDO calculations12 to be close

to stability in the corresponding cyclic dimers, have been observed

for lithium dibenzylamide (trimer),13 lithium hexamethyldisilazide

(tetramer),14 but only in the absence of coordinating solvents. In the presence

of ethereal solvents, lithium dibenzylamide and lithium hexa-

methyldisilazide form crystalline dimeric etherates, while lithium
tetramethylpiperidide forms etherates of unknown structure.

In addition, we recently described studies of the lithiated phe-

nylimine of cyclohexanone

(4), which is structurally quite similar

6Li NMR spectroscopic analyses of 0.015 M toluene-d₈ solutions of [6Li]Ph₂NLi at varying THF concentrations and ambient probe temperature showed single sharp resonances in the range of 0.05-0.19 ppm relative to a 0.30 M 6LiCl/methanol external standard. Cooling the probe to -90 °C caused signal overlap without an increase in spectral complexity. Overall, the spectral simplicity is consistent with virtually any structural form exhibiting either maximum possible symmetry or undergoing rapid chemical exchange on NMR timescales. To distinguish these two possibilities, we turned to 6Li-15N double labeling techniques.

Recent studies by Jackman and co-workers' and Collum and Kogler6 of 6Li doubly labeled compounds in conjunction with 6Li and 15N NMR spectroscopy for determining nitrogen-lithium connectivities of lithium amides and lithiated imines. By observing the spin -1/2 15N coupling to lithium by 6Li NMR spectroscopy, the number of nitrogens connected to lithium can be readily ascertained. Conversely, monitoring the spin 1 6Li coupling to nitrogen by 15N NMR spectroscopy15 provides the number of lithium atoms connected to each nitrogen. The combination of these results can distinguish monomeric, cyclic oligomeric, and ion triplet forms of lithium amides.

15N diphenylamine was prepared by trapping benzene with [15]Naniline. After exploring a number of procedures, we ultimately settled upon the preparation based on benzene diazonium carbonate depicted in eq 2. 
(Caution: benzene diazonium carbonate is highly explosive when fully dry.)

15N[NH₂]CO₂

70°C

12.3% yield

[6Li,15N]Ph₂NLi(solvent-free) was prepared and submitted to 6Li NMR spectroscopic analysis in 0.015 M toluene-d₈/THF solutions (Figure 1). The signal of Ph₂NLi at 0.16 ppm (0.15 M THF, 1.25%) appears as a 1:2:1 triplet (JLi-N = 3.12 Hz) showing equivalent coupling of lithium to two neighboring 15N nuclei (Figure 1a). As the THF concentrations were increased, coupling was lost, presumably due to rapid intermolecular exchange processes (Figure 1b). The complementary 15N NMR spectroscopic analysis of [6Li,15N]Ph₂NLi was also informative (Figure 1c). The lower sensitivity of the 15N nucleus required elevated Ph₂NLi concentrations (0.05 M, 0.15 M THF). The spectrum recorded at -90 °C displays a 1:2:3:2:1 pentuplet (JLi-N = 3.34 Hz) centered at 128.84 ppm. The multiplicity and the magnitude of the coupling constant are fully consistent with Li-N-Li connectivity.

Ph₂NLi: Structure at Low THF Concentrations. On the basis of the double labeling spectroscopic studies showing Li-N-Li and

References


(6) Suspensions of Ph₂NLi, solvent-free in benzene appeared to become homogeneous upon addition of only 0.8 equiv of THF per lithium. The 6Li NMR spectrum recorded at -90 °C displayed complex envelope of resonances.


Table 1. \(^{13}\)C (I'H) NMR Spectral Data of 0.015 M Toluene-\(d_8\) Solutions of Ph\(_2\)NLi\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>[THF], mol/L</th>
<th>temp, °C</th>
<th>ipso meta ortho para</th>
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<td>1</td>
<td>0.23</td>
<td>-90</td>
<td>159.89</td>
</tr>
<tr>
<td>2</td>
<td>0.26</td>
<td>23</td>
<td>b</td>
</tr>
<tr>
<td>3</td>
<td>0.26</td>
<td>-90</td>
<td>159.90</td>
</tr>
<tr>
<td>4</td>
<td>0.60 (5%)</td>
<td>-90</td>
<td>159.88, 158.92</td>
</tr>
<tr>
<td>5</td>
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<td>-90</td>
<td>158.89</td>
</tr>
<tr>
<td>6</td>
<td>4.43 (36%)</td>
<td>23</td>
<td>b</td>
</tr>
<tr>
<td>7</td>
<td>4.43</td>
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<tr>
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</tr>
<tr>
<td>9</td>
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<td>-90</td>
<td>159.04</td>
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</table>

\(^a\)The reported chemical shifts are in ppm relative to TMS. \(^b\)The ipso carbon resonances were poorly resolved from baseline noise at ambient temperature at convenient scan times. \(^c\)The resonance was obscured by the toluene-\(d_8\). \(^d\)THF-\(d_8\) was used as the solvent.

Figure 2. Observed molality of Ph\(_2\)NLi (0.21 M in monomer subunits) measured as a function of added THF. The solid lines represent calculated plots for models based on various solvated dimers as labeled.

Thus, we concur with Snaith and co-workers \(^16\) that the higher order cyclic oligomers might be restricted to ligand-free amides and assign the aggregated form of Ph\(_2\)NLi as a cyclic dimer of general structure 1. To assign the solvation state of Ph\(_2\)NLi, we turned to colligative studies of Ph\(_2\)NLi in benzene/THF mixtures.

Ph\(_2\)NLi\(_{\text{solvation-free}}\) was prepared from halide-free ethyllithium \(^\text{17}\) as shown in eq 1. Data on the solvation state of Ph\(_2\)NLi dimer solvated by THF were obtained by freezing point depression measurements. \(^18\) Figure 2 is a plot of measured molality as a function of added THF at a fixed concentration of Ph\(_2\)NLi\(_{\text{isolvent-free}}\). For each data point Ph\(_2\)NLi\(_{\text{isolvent-free}}\) was dissolved by adding 3.0 equiv of tetrahydrofuran per lithium. The dashed lines represent calculated plots for di-, tri-, and tetrasolvated dimers, respectively. The measured solution molalities correlated equally well with the theoretical lines for di- or tri-solvated dimers 1A or 1B.

Ph\(_2\)NLi: \(^{13}\)C NMR Spectroscopic Studies. We suspected that the high functionality of Ph\(_2\)NLi, evidenced by loss of Li-1\(^{15}\)N coupling at high THF concentration, obscured important THF concentration-dependent deaggregations. Indeed, the higher frequency of \(^{13}\)C NMR spectroscopy allowed direct detection of what we believe to be a dimer-monomer equilibrium (eq 3).


\(^{19}\) Control experiments showed solutions of free THF in benzene measured within 3% of the correct molalities. Because of both the phase behavior of benzene solutions of naphthalene and the nonlinearity of the electronics within the temperature probe, the standard curve shows gentle curvature over the range of solute concentration. Apparently, the benzene/THF solutions show similar (cancelling) curvature. In contrast, other solutes such as pyridine can result in a distinct error in the measured molality.

\[ \text{Ph}_2\text{NLi} + n \text{THF} \rightleftharpoons \text{Ph}_2\text{NLi(THF)}_n \]
The $^{13}$C NMR spectrum of a 0.015 M toluene-$d_8$ solution of Ph$_2$NLi contains 15 equiv of THF (0.26 M; 2.1%) at -90 °C displays four aromatic resonances and two resonances corresponding to the $\alpha$ and $\beta$ carbons of THF (Figure 4a, Table I). Exchange of bound and free THF molecules is rapid on the NMR timescales, and the high spectral symmetry is consistent with facile rotation about the C-N bonds. Increasing the THF concentration to 0.6 M (4.8%) affords a second species (Figure 4b), which becomes the sole observable species as the THF concentration exceeds 1.2 M (9.8%; Figure 4c). The equilibrium is also amide concentration dependent; decreasing the Ph$_2$NLi concentration 10-fold results in a significant decrease in the proportion of the dimer. The THF and Ph$_2$NLi concentration dependencies are fully consistent with a dimer-to-monomer deaggregation (eq 3).

Jackman and Scarmoutzos reported that a variety of lithiated aniline derivatives display temperature- and solvent-dependent $^{13}$C chemical shifts. Para carbon upfield shifts in the range of 4-5 ppm were attributed to increasing solvation with concomitant deaggregation to the monomeric state. Within any given aggregation state, upfield para carbon shifts of 1-2 ppm were ascribed to the electronic changes resulting from increased solvation. We do not now whether the Ph$_2$NLi monomer exists as di- or trisolvated contact ion pairs $3a$ and $3b$ or tetrasolvated solvent-separated ion pair $3c$. It is noted, however, that as the THF concentration is increased from 1.2 to 12.28 M (neat), the para carbon resonance of the monomeric Ph$_2$NLi shifts an additional 0.54 ppm upfield, indicative of either increasing monomer solvation or medium effects.

Ph$_2$NLi-LiBr: $^6$Li NMR Spectroscopic Studies. In the accompanying paper we will describe kinetic studies that uncovered autocatalysis by LiBr generated during the reaction of Ph$_2$NLi with n-butyl bromide. The role of the lithium bromide was traced to the intervention of a Ph$_2$NLi-LiBr mixed aggregate, which was characterized as follows.

Toluene-$d_8$ solutions of [Li]Ph$_2$NLi and [Li]Br in varying ratios were submitted to $^6$Li NMR analysis at -90 °C (Figure 5C). THF concentrations below 0.09 M were required to observe the limiting, slow exchange spectra. When the Ph$_2$NLi/LiBr ratio is <1.0, the resonance corresponding to the homonuclear Ph$_2$NLi dimer is observed at 0.16 ppm along with a resonance at 0.58 ppm corresponding to a Ph$_2$NLi-LiBr mixed aggregate (Figure 5a). At equimolar concentrations, the mixed aggregate is the only observable species (Figure 5b). In the presence of >1.0 equiv of LiBr, the resonance of the mixed aggregate is observed along with a resonance at 0.87 (Figure 5c) corresponding to free LiBr. At even moderately increased THF concentrations, the resonances corresponding to the mixed aggregate, the dimer, and LiBr become time averaged.

The stoichiometries clearly indicate that Ph$_2$NLi and LiBr form a 1:1 mixed aggregate quantitatively at low THF concentrations, with the equilibrium shifted substantially toward the mixed aggregate form. The atomic connectivity within the mixed aggregate was probed by using the $^6$Li-$^15$N double labeling techniques as described below.

Ph$_2$NLi-LiBr: $^6$Li and $^{15}$N Double Labeling Studies. The $^6$Li NMR spectrum of a 0.015 M toluene-$d_8$ solution of a 1:1 [Li]Ph$_2$NLi/LiBr mixture (-90 °C, 0.038 M THF) displays a doublet centered at 0.56 ppm (Figure 6a). The coupling pattern
The resonance was obscured by the toluene-d₈. The ipso carbon resonances were poorly resolved from base-line noise in the ambient temperature spectra recorded at convenient scan times.

Table II. ¹³C (H) NMR Spectral Data for Ph₂NLi/LiBr Mixtures*⁺

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<td>128.12</td>
<td>118.95</td>
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* The resonance was obscured by the toluene-d₈. ⁺ The ipso carbon resonances were poorly resolved from base-line noise in the ambient temperature spectra recorded at convenient scan times.

Figure 7. Observed molality measured as a function of added THF for suspensions of Ph₂NLi/LiBr (0.21 M) in benzene. The lines represent calculated plots for models based on dimers of varying solvation state as labeled.

demonstrates that each lithium is connected to only one ¹⁵N nucleus. Although this would be consistent with either a mixed dimer (cf. 2) or some variant of a monomeric amide, the 3.24-Hz coupling constant is well within the 3-4-Hz range previously observed for lithium amide dimers rather than the 6-7-Hz range observed for monomeric amides.¹⁴

The high fluctionality of Ph₂NLi.LiBr is apparent from the loss of coupling as the THF concentration exceeds 0.06 M. Unfortunately, at the elevated Ph₂NLi/LiBr and THF concentrations required for ¹⁵N NMR spectroscopic analysis, only poorly resolved coupling can be observed (Figure 6b). Nonetheless, on the basis of the observed 1:1 Ph₂NLi/LiBr stoichiometry, the ⁶Li NMR coupling pattern, and the magnitude of the observed coupling constant, the Ph₂NLi.LiBr mixed aggregate is assigned general structure 2 with reasonable confidence. The solvation state was determined cryoscopically as follows.

Ph₂NLi.LiBr: Colligative Studies. Figure 7 is a plot of observed molalities of benzene solutions of Ph₂NLi/LiBr as a function of added THF. Measurements recorded on heterogeneous mixtures from 0.0 to 3.0 equiv of THF were highly variable and are not displayed. Included in Figure 7 are calculated plots for the various solvation states of Ph₂NLi.LiBr as labeled. Figure 8 is a plot of measured molality as a function of the absolute concentration of Ph₂NLi.LiBr. For each data point solvent-free Ph₂NLi/LiBr was dissolved by adding 3.0 equiv of THF per lithium atom.

Ph₂NLi.LiBr: Structure at Low THF Concentrations. Corroboration evidence from the two colligative experiments taken in conjunction with the spectroscopic evidence supports trisolvated mixed dimer 2a as the most likely solution structural form of Ph₂NLi.LiBr.²¹ One of the more curious features of 2a is the unsymmetrical tris solvation state. Jackman has discussed in some detail the possibility of equilibria between di-, tri-, and tetrasolvated amide dimers in the context of condition-dependent ¹³C chemical shifts.² However, to the best of our knowledge a lithiated di- or some variant of a monomeric amide, the 3.24-Hz coupling as the THF concentration exceeds 0.06 M. Unfortunately, at the elevated THF concentrations eq 4) in analogy to the Ph₂NLi dimer (eq 3). Although the high fluctionality of Ph₂NLi.LiBr precluded ⁶Li NMR spectroscopic studies, the higher frequency of ¹³C NMR spectroscopy once again proved advantageous.

2:1 mixtures of Ph₂NLi and LiBr were monitored over a large portion of the THF concentration range (Figure 9, Table II). The Ph₂NLi dimer and Ph₂NLi.LiBr are fully resolved at 0.26 M THF (Figure 9a). As the THF concentration increases, the resonances


(23) As drawn, the asymmetry of such tri solvates would not be expected to be observable by NMR spectroscopy due to high solvent exchange rates. Sharp, H. J.; Symons, M. C. R. In Ions and Ion Pairs in Organic Reactions; Srawe, M., Ed.; Wiley: New York, 1972; Vol. 1, Chapter 15. Jackman, L. M.; DeBrosse, C. W. J. Am. Chem. Soc. 1983, 105, 4177. As noted by one referee, a single 1a-azaallyl lithium interaction could cause the preference for tris solvation.
Structure and Reactivity of Lithium Amides

An increase in the concentration of the mixed aggregate. The I3C resonances corresponding to the Ph2NLi monomer and of Ph2NLi/LiBr.

The structural forms in the presence and absence of LiBr, then one Ph,NLi.LiBr dissociates to monomer and free LiBr as depicted in eq 4. This ambiguity will be further highlighted in the accompanying paper.

Summary and Conclusions

The conclusions from the spectroscopic and colligative studies are summarized in Scheme I.

At low THF concentrations 6Li and 15N NMR spectroscopic analyses revealed that Ph2NLi exists in a cyclic aggregate form. Although cyclic dimers, trimers, and tetramers cannot be distinguished from the 6Li-15N coupling patterns alone, strong arguments and structural analogies support a dimer structure. Within the constraints imposed by the assignment of Ph2NLi as a cyclic dimer, the colligative measurements are consistent with either a di- or trisolvate (1a or 1b).

As the THF concentrations were increased, rapid fluctuational processes rendered the powerful 1H and 6Li NMR spectroscopic probes completely ineffective. Nonetheless, dissociation of dimer 1 to monomer 3 was observed directly by 13C NMR spectroscopy, although details of the monomer structure and solvation state remain obscure.

4Li and 15N NMR spectroscopic studies and colligative measurements of Ph2NLi/LiBr mixtures at low THF concentrations demonstrated the presence of mixed aggregate 2a in a rarely observed, unsymmetrical trisolvation state. 13C NMR spectral studies of Ph2NLi/LiBr mixtures showed the Ph2NLi-LiBr mixed aggregate to be involved in slow exchange with dimeric Ph2NLi and rapid exchange with monomeric Ph2NLi. Despite substantial losses in structural information arising from the high fluctuational effects of LiBr on the time-averaged 13C chemical shifts of Ph2NLi, we cannot, however, rigorously exclude the existence of such species as ion triplet 5 at high THF concentrations.

In the following paper, we will describe kinetic studies of the N-alkylation of Ph2NLi with n-BuBr. Although some of these structural issues remain unresolved, the kinetic data demonstrate the role of solvation and the importance of homo- and heteronuclear aggregates, monomers, and free ions as contributors to the reactivity of lithium amides.

Experimental Section

General Procedures. Benzenes, tetrachlorofuran (THF), and all deuterated solvents were distilled from blue or purple solutions containing sodium benzophenone ketyl under vacuum. The hydrocarbon solvents contained 1% tetrachloromethane to dissolve the ketyl. The benzene used in the molecular weight determinations was distilled from LiAlH4. 6Li metal (95.5%) was obtained from Oak Ridge National Laboratory. Ethyl lithium and [6Li]ethyl lithium were prepared by the standard literature procedures.

The solutions of Ph2NLi/LiBr were recrystallized from hexane. and free LiBr at intermediate and high THF concentrations. However, ion triplet 5 cannot be rigorously excluded as a plausible solution structural form.

In the following paper, we will describe kinetic studies of the N-alkylation of Ph2NLi with n-BuBr. Although some of these structural issues remain unresolved, the kinetic data demonstrate the role of solvation and the importance of homo- and heteronuclear aggregates, monomers, and free ions as contributors to the reactivity of lithium amides.
and 40.53 MHz, respectively. $^1$H NMR spectra were recorded on a Varian XL-200 spectrometer. $^1$H and $^{13}$C NMR shifts are reported in ppm downfield of tetramethylsilane. The $^1$H chemical shifts are reported in ppm relative to an external 0.3 M $\text{LiCl}$/methanol standard. The $^{13}$C chemical shifts are reported in ppm relative to an external 0.15 M $[^{15}$N]$\text{d}_{2}$amylene/THF standard set at 50 ppm. NMR probe temperatures are accurate to $\pm 0.2^\circ \text{C}$.

The following is a representative procedure for preparing samples for spectroscopic analysis. A stock solution was prepared in a glovebox by sequentially mixing $[^{6}$Li,$^{13}$C]$\text{Ph}_{2}$NLi with toluene-$d_8$ (840 µL), and THF (31 µL). The tube was placed under septum, removed from the glovebox, and sealed with a flame under reduced pressure.

Colligative Measurements. Solution molalities were measured by freezing-point depression by using a modification of an apparatus described by Seebach$^7$ interfaced to a Commodore 64 or VIC-20 mini-computer. Samples were prepared in a glovebox and measurements were made under $N_2$ with standard inert atmosphere techniques. Calibrations were performed with known concentrations of naphthalene in benzene.

$[^{15}$N]$\text{Ph}_{2}$NLi solvent-free. The various isomers of solvent-free lithium diphenylamide were prepared as follows. A 500-mL round-bottom flask fitted to a glass filter frit was charged with diphenylamine (5.27 g, 31.1 mmol) and ethyllithium (1.18 g, 32.8 mmol). To this was added 300 mL of a 2:1 hexane/diethyl ether mixture via vacuum transfer at $-78^\circ \text{C}$. The milky white solution was warmed to 0 $^\circ \text{C}$ and stirred for 1.5 h. The resultant clear solution was concentrated in vacuo to 80 mL and then cooled to $-78^\circ \text{C}$. Filtration afforded an off-white solid, which was recrystallized from hexane at $-78^\circ \text{C}$.

Structure and Reactivity of Lithium Diphenylamide. Role of Aggregates, Mixed Aggregates, Monomers, and Free Ions on the Rates and Selectivities of N-Alkylation and E2 Elimination

Jeffrey S. DePue and David B. Collum*

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301. Received January 11, 1988

Abstract: Rate studies of the N-alkylation of lithium diphenylamide with n-butyl bromide in THF/hydrocarbon mixtures (THF = tetrahydrofuran) are described. Dramatic induction periods observed for the N-alkylation at low THF concentrations are ascribed to the intervention of reactive mixed dimers of lithium diphenylamide and lithium bromide. In the presence of 1.0 equiv of added lithium bromide, the alkylation rate exhibits a first-order dependence on both the mixed aggregate and n-butyl bromide concentrations, supporting a pathway involving direct mixed aggregate alkylation. Incremental changes in the THF concentration uncovered contributions from several additional species. Regions of first or higher order followed by zero-order dependence on the THF concentration are interpreted as an equilibrium shift to a more reactive, highly solvated species assigned as a monomer (or ion pair). At elevated THF concentrations, the alkylation rate increases sharply as a function of the THF concentration, indicating the contribution of an additional, highly solvent dependent alkylation pathway. This latter pathway exhibits fractional-order dependence on the amide concentration, approximate first order dependence on the n-butyl bromide concentration, and a seventh-order dependence on the THF concentration. Common ion rate inhibitions by lithium perchlorate and lithium tetraphenylborate, a significant dependence on dielectric effects, and the observed reaction order dependence on lithium ion concentration implicate a mechanism involving preassociation of free lithium ions. The appearance of competitive eliminations of the n-alkyl bromides to form 1-alkenes coincides with the appearance of the free ion alkylation pathway.

Lithium dialkylamides are used routinely throughout organic chemistry as highly reactive and selective bases. Elegant quantitative studies of lithium amides include Streitwieser$^1$s and Fraser$^2$s ion pair acidity measurements, Newcomb$^3$s investigations of amide-mediated hydride transfer, and Huigen$^4$s extensive studies of dehydrohalogenations of aryl halides. However, most