

Table I. Dediazonation of 1×10^{-4} M 16-ArN₂⁺ in 0.01 M CTABr and 0.01 M HBr with Added BuOH at 40 ± 0.1 °C^a Normalized Product Yields of 16-ArOH, 16-ArBr, and 16-ArOBu^b

[BuOH], M	% yield 16-ArOH	% yield 16-ArBr	% yield 16-ArOBu
0.000	72.9	27.1	
0.100	75.6	22.6	1.8
0.219	78.9	18.2	3.0
0.437	83.6	11.8	4.6
0.656	87.0	7.3	5.8
0.765	88.0	5.7	6.3
0.874	88.5	4.7	6.8

^a Reaction is initiated by injection of 50 μL of 0.01 M 16-ArN₂⁺ in MeCN into a 5-mL thermally equilibrated volumetric containing the needed reagents. After >10 half-lives (about 325 min), large aliquots are injected into the HPLC, overfilling the injector loop. ^b HPLC peak areas, measured % yields, and calibration curves are in Table S1.

microenvironment of the diazonium salt ground state in equilibrium with its surroundings. Thus, product distributions from reaction of 1-ArN₂⁺ in aqueous solution are proportional to stoichiometric nucleophile concentrations, and product distributions from reaction of hydrophobic 16-ArN₂⁺ bound to aggregates are a "snapshot" of interfacial nucleophile composition.⁷

Table I gives a typical reaction protocol for dediazonation of 16-ArN₂⁺ and the normalized mole percent yields of products.⁹ Product yields are calculated from HPLC peak areas by using calibration curves obtained with independently synthesized products. Figure 2 shows Y_m values as a function of added BuOH calculated from product yields in Table I and the selectivity of 1-ArN₂⁺ in aqueous solution toward Br⁻, S_w^{Br}, and BuOH, S_w^{BuOH}, compared to water over wide ranges of [NaBr] and [BuOH], respectively.¹⁰ The calculation of Y_m is based on our assumption that the selectivities of 16-ArN₂⁺ in microemulsions and 1-ArN₂⁺ in aqueous solution toward different nucleophiles are the same; e.g., when the yields of 16-ArBr (in microemulsions) and 1-ArBr (in aqueous solution) are the same, Br⁻_m (in microemulsions) = [NaBr] (in aqueous solution).

Added BuOH displaces both Br⁻ and H₂O from the interfacial region (Figure 2). At the highest [BuOH], 0.87 M, just below its solubility limit in 0.01 M CTABr,^{8a} BuOH_m ≈ 10. We estimate the concentration of bound BuOH to be ca. 8 mol/L of total aggregate volume at [BuOH] = 0.87 M from its binding constant, $K = 1 \text{ M}^{-1}$,^{8a} and by assuming that the volumes of aggregated CTABr and BuOH are additive. As BuOH_m increases from 0 to 10 with added BuOH, there is a concomitant decrease in H₂O_m from 50 to 37, indicating an approximately 1:1 exchange of BuOH for H₂O in the interfacial region. However, % 16-ArOH increases modestly (Table I) because the dediazonation reaction is less selective toward BuOH than Br⁻, i.e., S_w^{BuOH} < S_w^{Br}.¹⁰ At [BuOH] = 0, Br⁻_m = 2.30, slightly below literature estimates of 3–5 mol/L of interfacial volume³ and our previous estimate of 3.3 in 0.01 M CTABr, 0.1 M HBr (10 times greater than the [HBr] here), using a different diazonium salt.⁴ The decrease in Br⁻_m with added BuOH parallels the drop in the fraction of Br⁻ bound to myristyltrimethylammonium bromide micelles with added BuOH.¹¹

(7) 16-ArN₂⁺ is assumed to be completely microemulsion bound.⁴ It is water insoluble and more hydrophobic than CTABr, added BuOH reduces the cmc of CTABr,¹¹ and the CTABr monomer concentration is always <10% of total [CTABr] (at 40 °C, CTABr's cmc = 1.08×10^{-3} M in the absence of added salt^{8b}).

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(9) Details on the preparation and dediazonation rates of the tetrafluoroborate salts of 16-ArN₂⁺ and 1-ArN₂⁺ are in Appendix S1. Normalized mole percent product yields are reported because the measured product yields range from 87 to 100% and the HPLC chromatograms are free of stray peaks (>1%).

(10) Selectivities S_w^{Br} = 8.3 and S_w^{BuOH} = 0.31 were determined by standard methods (Appendix S2).⁴ Tables S1–S3 give product yields and calibration data for z-ArN₂⁺.

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Our dediazonation reaction is an excellent probe of association colloid interfaces. It distinguishes between chemically similar nucleophiles (e.g., Cl⁻ and Br⁻;⁴ H₂O and BuOH), and it can be used with all weakly basic nucleophiles which react by the same mechanism⁵ over a wide range of solution compositions. Future results should provide new information on the interfacial compositions of three- and four-component microemulsions.¹

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Supplementary Material Available: Appendices S1 and S2, detailing diazonium salt preparation, dediazonation kinetics, and the procedure for calculating interfacial concentrations of H₂O, BuOH, and Br⁻, and Tables S1–S3, providing product yields and HPLC calibration data for dediazonations of 16-ArN₂⁺ and 1-ArN₂⁺ (6 pages). Ordering information is given on any current masthead page.

Lithium Diisopropylamide Mixed Aggregates: Structures and Consequences on the Stereochemistry of Ketone Enolate Formation

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Stereochemical and regiochemical studies of ketone enolization by lithium dialkylamides have elicited extensive mechanistic discussions that typically invoke kinetic pathways in competition with enolate equilibrations.^{1–4} Noticeably absent from most (but not all)⁵ treatments are the possible roles of mixed aggregates and autocatalysis as determinants of selectivity and reactivity.⁶ Where

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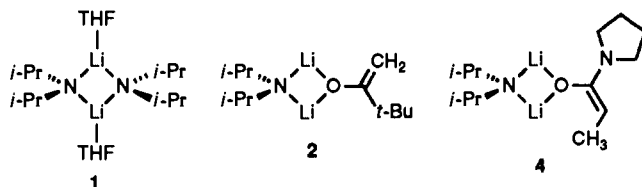
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lithium amide mixed aggregation effects are reported either implicitly or explicitly,^{5,6} structural details are lacking.⁷ Insights into lithium amide/lithium enolate mixed aggregate structures stem primarily from the crystallographic studies of Williard and co-workers.⁸

We describe solution structural studies demonstrating that lithium enolates display structure-dependent propensities to form 1:1 mixed dimers with LDA and that LiCl and LDA combine to form both 2:1 and 1:1 mixed aggregates. LiCl has a substantial effect on the stereochemistry of LDA-mediated enolizations.

Previous spectroscopic studies demonstrate that LDA exists exclusively as a cyclic oligomer (strongly suggested to be disolvated dimer 1).⁹ When [⁶Li,¹⁵N]LDA¹⁰ is treated with 1.0 equiv of [⁶Li]lithium pinacolate,¹⁰⁻¹² the ⁶Li NMR spectrum shows a doublet indicative of coupling to one neighboring spin 1/2 ¹⁵N nucleus (Figure 1A) along with the resonances corresponding to [⁶Li,¹⁵N]LDA and two previously¹² studied aggregates of free enolate.^{13,14} The corresponding ¹⁵N spectrum displays a new quintet along with the quintet of [⁶Li,¹⁵N]LDA (⁶Li; spin 1).¹⁴ The multiplicities are fully consistent with formation of limited concentrations of mixed dimer 2. The (*Z*)-lithium enolate of pyrrolidine propionamide (3)¹¹ affords limited concentrations of 1:1 mixed aggregate 4.¹⁴ In striking contrast, addition of 1.0 equiv of [⁶Li]lithium cyclohexenolate¹¹ to [⁶Li,¹⁵N]LDA affords ⁶Li and ¹⁵N NMR spectra showing no evidence of a mixed aggregate.



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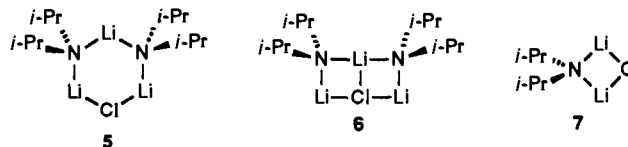
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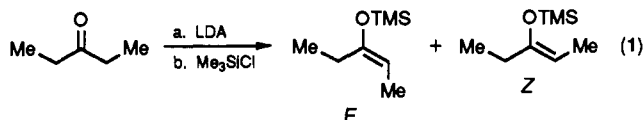
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(14) Pertinent NMR data recorded on solutions contained in 75% THF/pentane at -115 °C. The ⁶Li and ¹⁵N resonances are referenced to 0.3 M [⁶Li]LiCl/MeOH (0.0 ppm) and [¹⁵N]aniline (52 ppm) as described previously.¹³ 2: ⁶Li NMR δ 0.63 (d, *J*_{Li-N} = 4.9 Hz) ppm; ¹⁵N NMR δ 75.4 (quintet, *J*_{Li-N} = 4.8 Hz) ppm. 3: ⁶Li NMR δ 0.32 (s), 0.05 (s, minor), -0.15 (s) ppm. 4: ⁶Li NMR δ 0.74 (d, *J*_{Li-N} = 5.2 Hz) ppm; ¹⁵N NMR δ 77.9 (quintet, *J*_{Li-N} = 5.2 Hz) ppm. 5: ⁶Li NMR δ 2.24 (t, *J*_{Li-N} = 5.9 Hz, 1 Li), 0.70 (d, *J*_{Li-N} = 4.8 Hz, 2 Li) ppm; ¹⁵N NMR δ 78.3 (tt, *J*_{Li-N} = 5.9, 4.8 Hz) ppm. 7: ⁶Li NMR δ 0.62 (d, *J*_{Li-N} = 4.9 Hz) ppm; ¹⁵N NMR δ 77.9 (quintet, *J*_{Li-N} = 4.9 Hz) ppm.

Due to the increasingly popular use of lithium amide/R₃SiCl mixtures to effect lithiations,¹⁵ we investigated the influence of the LiCl generated in situ on the LDA solution structure. The ⁶Li NMR spectra of [⁶Li,¹⁵N]LDA/[⁶Li]LiCl mixtures at low [LiCl] display a resonance corresponding to LDA along with a new doublet and triplet in a 2:1 ratio (Figure 1B).¹⁶ A single new ¹⁵N triplet of triplets in the ¹⁵N NMR spectrum indicating coupling to two inequivalent ⁶Li nuclei provides the additional information necessary to assign the mixed aggregate as a 2:1 LDA/LiCl mixed cyclic trimer 5. We hasten to add that the alternative ladder 6 is a distinct structural possibility and derives substantial support from lithium amide/lithium enolate mixed aggregate ladder structures.^{8,17} At higher [LiCl], one observes a new ⁶Li doublet (Figure 1C) and ¹⁵N quintet fully consistent with mixed dimer 7.



Stereochemical studies on 3-pentanone enolization¹⁻⁴ reveal possible consequences of mixed aggregation (eq 1). A slight decrease in *E/Z* selectivity is observed with increasing percent conversion, consistent with either partial enolate equilibration^{4,18} or the intervention of enolate/LDA mixed aggregates (Figure 2). Addition of pinacolone enolate or enolate 3 (0.1-2.0 equiv) prior to the addition of the 3-pentanone (0.9 equiv) produces minimal stereochemical changes. In contrast, LiCl shows a pronounced effect on the *E/Z* selectivity, with a sharp maximum in selectivity appearing at approximately 0.3 equiv (Figure 3). Whether this is a consequence of mixed aggregate based enolization or some form of electrophilic catalysis¹⁹ remains to be determined.



In summary, the tendency of LDA to form mixed aggregates

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(16) A relatively minor yet reproducible triplet is visible (δ 2.39 ppm, *J*_{Li-N} = 6.1 Hz) in the ⁶Li NMR spectrum at low LiCl concentrations (Figure 1C). Concentration studies show it to be nonisomeric to either the 2:1 or 1:1 mixed aggregates 5 and 7, quite possibly possessing an LDA/LiCl ratio ≥ 3. The absence of a detectable ¹⁵N resonance, however, renders a structural assignment and further discussion unproductive at this time.

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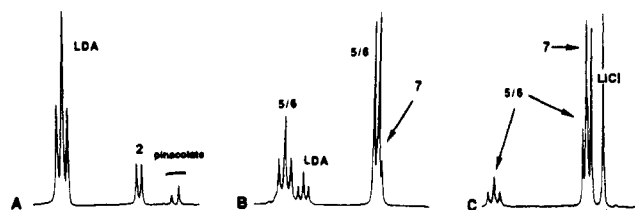


Figure 1. ^6Li NMR spectra of 0.1 M $[^6\text{Li},^{15}\text{N}]\text{LDA}$ in 3:1 THF/pentane at $-115\text{ }^\circ\text{C}$: (A) with 0.5 equiv of $[^6\text{Li}]\text{pinacolate}$; (B) with 0.4 equiv of $[^6\text{Li}]\text{LiCl}$; (C) with 1.5 equiv of $[^6\text{Li}]\text{LiCl}$. The spins of ^6Li and ^{15}N are 1 and $1/2$, respectively.

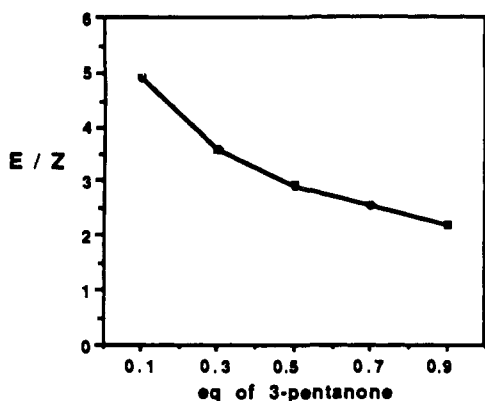


Figure 2.

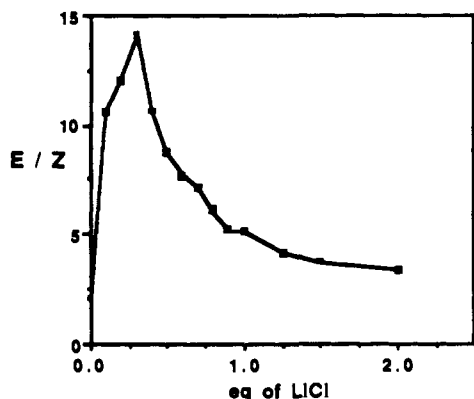


Figure 3.

with ketone enolates is both limited and structure dependent, but still may be of some practical consequence. The corresponding LDA/LiCl mixed aggregates are also observable and may have a substantial impact on the selectivity and reactivity of LDA. However, the approximate correlation of optimal concentrations of mixed aggregate **5** with maximal selectivities *must* be illusory; the continuously changing proportions of LDA, lithium enolate, and LiCl throughout the course of the enolization would result in a continuously changing structure distribution. Furthermore, studies of lithium 2,2,6,6-tetramethylpiperidine reveal that added lithium salts can have a substantially greater (and more complex) influence on the structures and reactivities of highly hindered lithium amides.²⁰

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Support for a Dimer of Di- μ -oxo Dimers Model for the Photosystem II Manganese Aggregate. Synthesis and Properties of $[(\text{Mn}_2\text{O}_2)_2(\text{tphpn})_2](\text{ClO}_4)_4$ ¹

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The task of elucidating the structure of the manganese aggregate in the oxygen-evolving complex of photosystem II (MnOEC), generally assumed to be the catalytic site of photosynthetic water oxidation, provides an interesting challenge for bioinorganic and biophysical chemists.²⁻⁶ Characteristics of this active-site complex include (i) a nuclearity of three or four manganese atoms, (ii) a broad low-field parallel polarization mode EPR absorption ($g_{\text{eff}} = 4.8$) at the S_1 oxidation level,⁴ (iii) multiline (19–21 lines, $g_{\text{eff}} = 2$) and $g_{\text{eff}} = 4.1$ EPR signals at the S_2 oxidation level,^{2,3} and (iv) at least two relatively short range Mn...Mn contacts (2.7 Å) as indicated by X-ray absorption spectroscopy.^{3,5,7} Furthermore, a peak in the Fourier transformed EXAFS data for MnOEC has been assigned to a 3.3-Å Mn...Mn interaction.^{5,7}

Complexes that contain the $\{\text{Mn}_2\text{O}_2\}^{3+}$ core⁶ may be viewed as preliminary or "first-generation" models for the MnOEC because they possess Mn...Mn distances of 2.7 Å and 16-line EPR spectra. However, the aforementioned binuclear complexes are not fully

(1) Abbreviations used: tphpn = *N,N,N',N'*-tetrakis(2-pyridylmethyl)-2-hydroxypropane-1,3-diamine, MnOEC = manganese aggregate in the oxygen-evolving complex of Photosystem II, EXAFS = extended X-ray absorption fine structure, EPR = electron paramagnetic resonance.

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