Table I. Dediazoniation of 1×10^{-4} M 16-ArN_2^+ 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-ArN_2^+ 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-ArN_2^+ in aqueous solution are proportional to stoichiometric nucleophile concentrations, and product distributions from reaction of hydrophobic 16-ArN_2^+ bound to aggregates are a "snapshot" of interfacial nucleophile composition.[7]

Table I gives a typical reaction protocol for dediazoniation of 16-ArN_2^+ 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-ArN_2^+ 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-ArN_2^+ in microemulsions and 1-ArN_2^+ 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 H_2O from the interfacial region (Figure 2). At the highest [BuOH], 0.87 M, just below its solubility limit in 0.01 M CTABr,[8a] $BuOH_m \cong 10$. 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, $K = 1\ M^{-1}$,[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 H_2O_m from 50 to 37, indicating an approximately 1:1 exchange of BuOH for H_2O in the interfacial region. However, % 16-ArOH increases modestly (Table I) because the dediazoniation 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 volume[3] 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-ArN_2^+ 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 dediazoniation rates of the tetrafluoroborate salts of 16-ArN_2^+ and 1-ArN_2^+ 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-ArN_2^+.

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Our dediazoniation reaction is an excellent probe of association colloid interfaces. It distinguishes between chemically similar nucleophiles (e.g., Cl^- and Br^-;[4] H_2O and BuOH), and it can be used with all weakly basic nucleophiles which react by the same mechanism[5] 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, dediazoniation kinetics, and the procedure for calculating interfacial concentrations of H_2O, BuOH, and Br^-, and Tables S1-S3, providing product yields and HPLC calibration data for dediazoniations of 16-ArN_2^+ and 1-ArN_2^+ (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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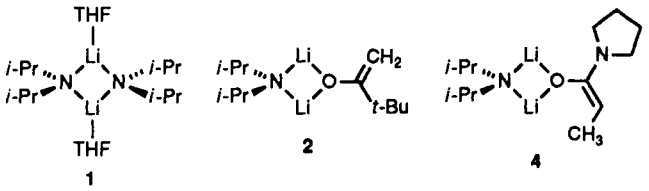
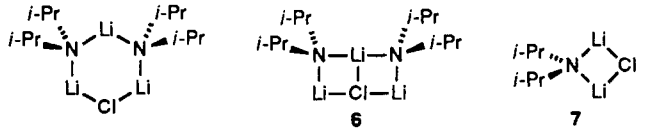
lithium amide mixed aggregation effects are reported either implicitly or explicitly,[5,6] structural details are lacking.[7] Insights into lithium amide/lithium enolate mixed aggregate structures stem primarily from the crystallographic studies of Williard and co-workers.[8]

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.

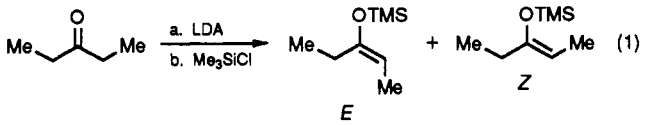
Previous spectroscopic studies demonstrate that LDA exists exclusively as a cyclic oligomer (strongly suggested to be disolvated dimer **1**).[9] When [^{6}Li,^{15}N]LDA[10] is treated with 1.0 equiv of [^{6}Li]lithium pinacolate,[10-12] the ^{6}Li NMR spectrum shows a doublet indicative of coupling to one neighboring spin $^1/_2$ ^{15}N nucleus (Figure 1A) along with the resonances corresponding to [^{6}Li,^{15}N]LDA and two previously[12] studied aggregates of free enolate.[13,14] The corresponding ^{15}N spectrum displays a new quintet along with the quintet of [^{6}Li,^{15}N]LDA (^{6}Li; 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 [^{6}Li]lithium cyclohexenolate[11] to [^{6}Li,^{15}N]LDA affords ^{6}Li and ^{15}N NMR spectra showing no evidence of a mixed aggregate.



Due to the increasingly popular use of lithium amide/R_3SiCl mixtures to effect lithiations,[15] we investigated the influence of the LiCl generated in situ on the LDA solution structure. The ^{6}Li NMR spectra of [^{6}Li,^{15}N]LDA/[^{6}Li]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 ^{15}N triplet of triplets in the ^{15}N NMR spectrum indicating coupling to two inequivalent ^{6}Li 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 ^{6}Li doublet (Figure 1C) and ^{15}N quintet fully consistent with mixed dimer **7**.



Stereochemical studies on 3-pentanone enolization[1-4] 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 catalysis[19] remains to be determined.



In summary, the tendency of LDA to form mixed aggregates

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

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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 ^{6}Li 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 ^{15}N resonance, however, renders a structural assignment and further discussion unproductive at this time.

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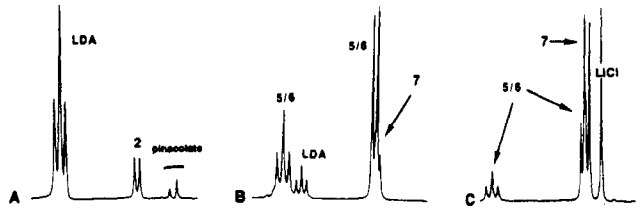

Figure 1. ^{6}Li NMR spectra of 0.1 M [^{6}Li,^{15}N]LDA in 3:1 THF/pentane at −115 °C: (A) with 0.5 equiv of [^{6}Li]pinacolate; (B) with 0.4 equiv of [^{6}Li]LiCl; (C) with 1.5 equiv of [^{6}Li]LiCl. The spins of ^{6}Li and ^{15}N are 1 and $^1/_2$, respectively.

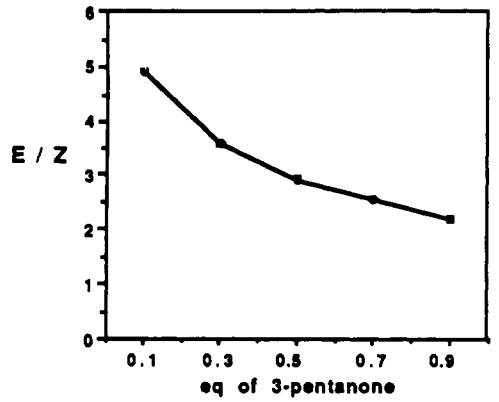

Figure 2.

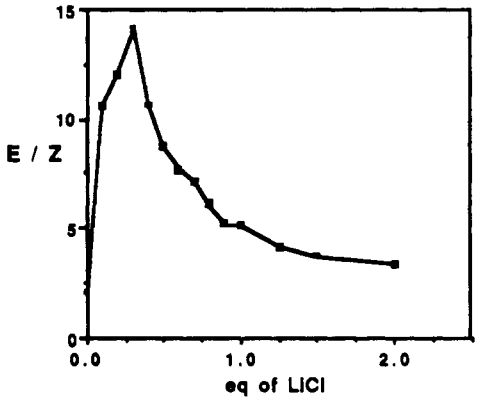

Figure 3.

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-tetramethylpiperidide 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 $[(Mn_2O_2)_2(tphpn)_2](ClO_4)_4$[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_{eff} = 4.8) at the S_1 oxidation level,[4] (iii) multiline (19–21 lines, g_{eff} = 2) and g_{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 $\{Mn_2O_2\}^{3+}$ core[6] 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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