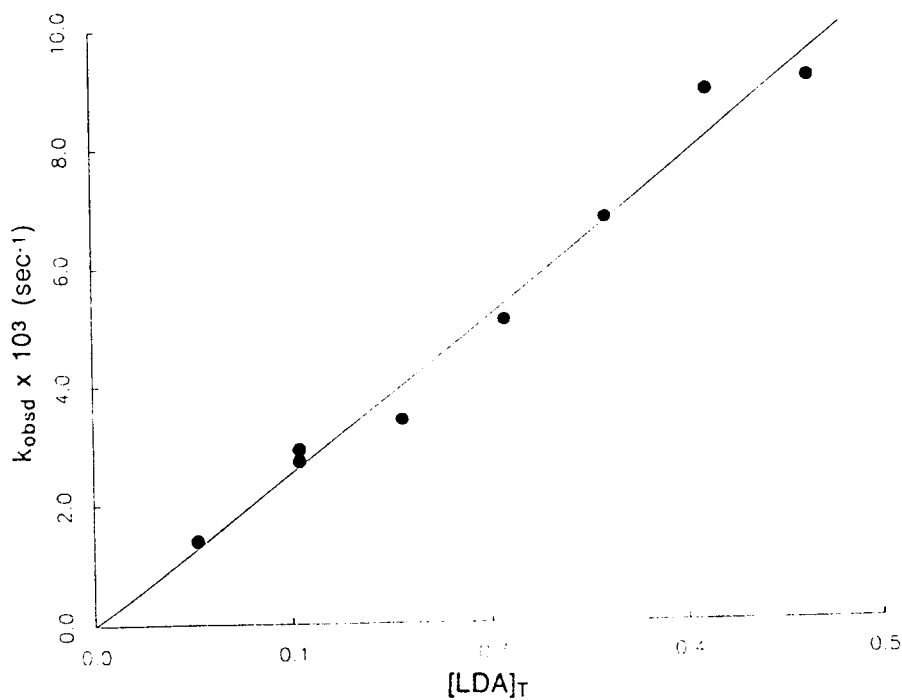


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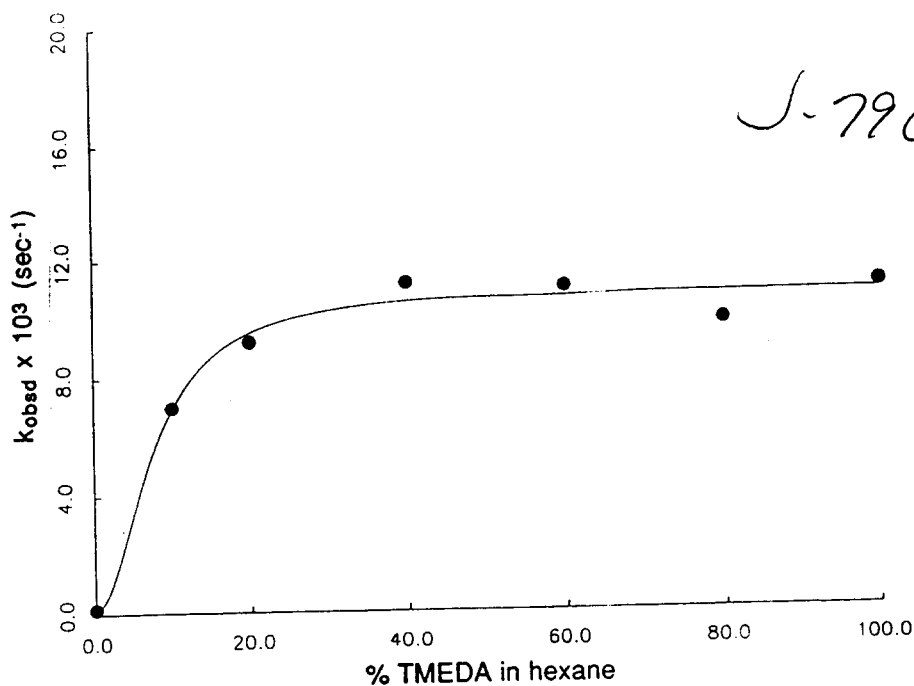
Supplementary Material for

Metallation of Imines by Lithium Diisopropylamide (LDA) Solvated
by
N,N,N',N'-Tetramethylethylenediamine (TMEDA):
Evidence for Solvent-Free Open Dimer Reactive Intermediates.

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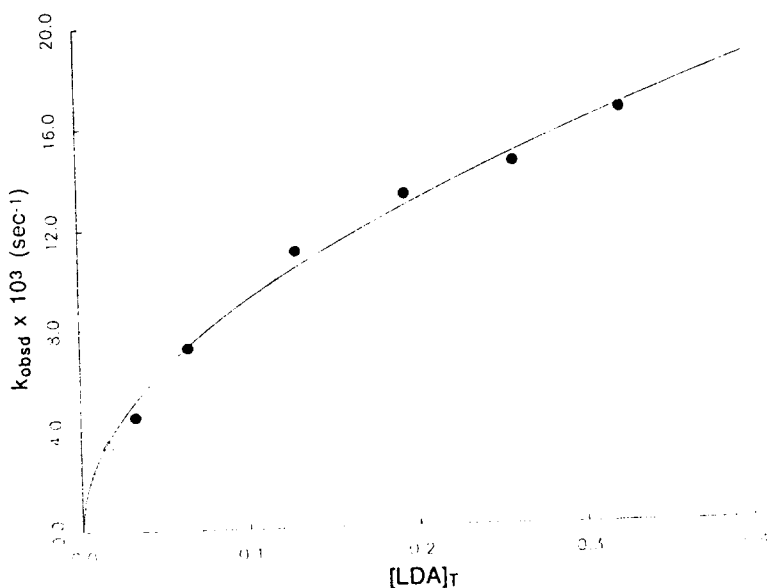
Plot of k_{obsd} versus [LDA] in neat TMEDA for the metallation of imine **3** (0.004 M) at 0.0 ± 0.5 °C. The curve depicts the result of an unweighted, non-linear least squares fit to the general expression $k_{\text{obsd}} = k'[\text{LDA}]^n$ ($n = 1.06 \pm 0.03$).



Plot of k_{obsd} versus [TMEDA] in hexane co-solvent for the metallation of imine 2- d_4 (0.004 M) by LDA (0.13 M) at 0.0 ± 0.5 °C. The curve depicts the result of an unweighted, non-linear least squares fit to the previously described (Bernstein *et al.*, see below) general expression

$$k_{\text{obs}} = a[\text{TMEDA}]/(1 + ab[\text{TMEDA}]) + c$$

such that a and b are adjustable parameters corresponding to rate and equilibrium constants, and c is an adjustable parameter corresponding to the slight non-zero rate in the absence of TMEDA. The fall-off in rates below 30% by volume TMEDA was shown previously to coincide with the desolvation of the LDA (Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q.-Y.; Williard, P. G. *J. Am. Chem. Soc.* 1992, 114, 5100).



Plot of k_{obsd} versus [LDA] in neat TMEDA for the metallation of imine 2- d_4 (0.004 M) at 0.0 ± 0.5 °C. The curve depicts the result of an unweighted non-linear least squares fit to the general expression $k_{\text{obsd}} = k'[\text{LDA}]^n$ ($n = 0.51 \pm 0.01$). The rate constant at the lowest LDA concentrations designated by a triangle (Δ) was not recorded under fully pseudo-first-order conditions and was not included in the fit.