University of Missouri-Columbia
Department of Chemistry
Organic Cume, May 14, 2005
Dr. Rainer Glaser

Chelation Effects in Carbanion Chemistry

Suggested Reading:

[1] *The Regioselectivity of Addition of Organolithium Reagents to Enones and Enals: The Role of HMPA* Sikorski, W. H.; Reich, H. J. *J. Am. Chem. Soc.* **2001**, *123*, 6527-6535.

[2] The Effect of HMPA on the Reactivity of Epoxides, Aziridines, and Alkyl Halides with Organolithium Reagents Reich, H. J.; Sanders, A. W.; Fiedler, A. T.; Bevan, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 13386-13387.

[3] Amine- and Ether-Chelated Aryllithium Reagents-Structure and Dynamics Reich, H. J.; Goldenberg, W. S.; Sanders, A. W.; Jantzi, K. L.; Tzschucke, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 3509-3521.

Question 1. Provide brief and concise definitions for each term. State what each abbreviation stands for (spell it out) and explain what that means. For abbreviations that refer to chemicals, give the full name, the structure, and the function. (20 points)

CIP
SIP
HMPA
DMPU
PMDTA

Chelation Isomers
THF
[^{17}O]-THF
Magnetogyric Ratio
1,4-Addition

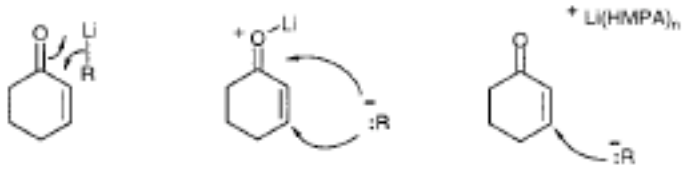
Question 2. HMPA in 1,2- and 1,4-Addition Chemistry. (25 points)

(a) Explain why HMPA accelerates organolithium reactions in THF. (6 points)

(b) Draw the major products formed by reaction of lithiated 1,3-disulfa-cyclohexane to cyclohexenone in the presence and absence of HMPA. (10 p.)

(c) Part of Scheme 2 of ref. 1 is reproduced. Explain in your own words what this scheme is supposed to show. (9 points)

Scheme 2. Mechanistic Proposal



Question 3. Amine- and Ether-Chelated Aryllithium Reagents. (30 points)

(a) Draw the structures. (6 points)

2-(2-dimethylaminoethyl)phenyllithium	2-(methoxymethyl)phenyllithium

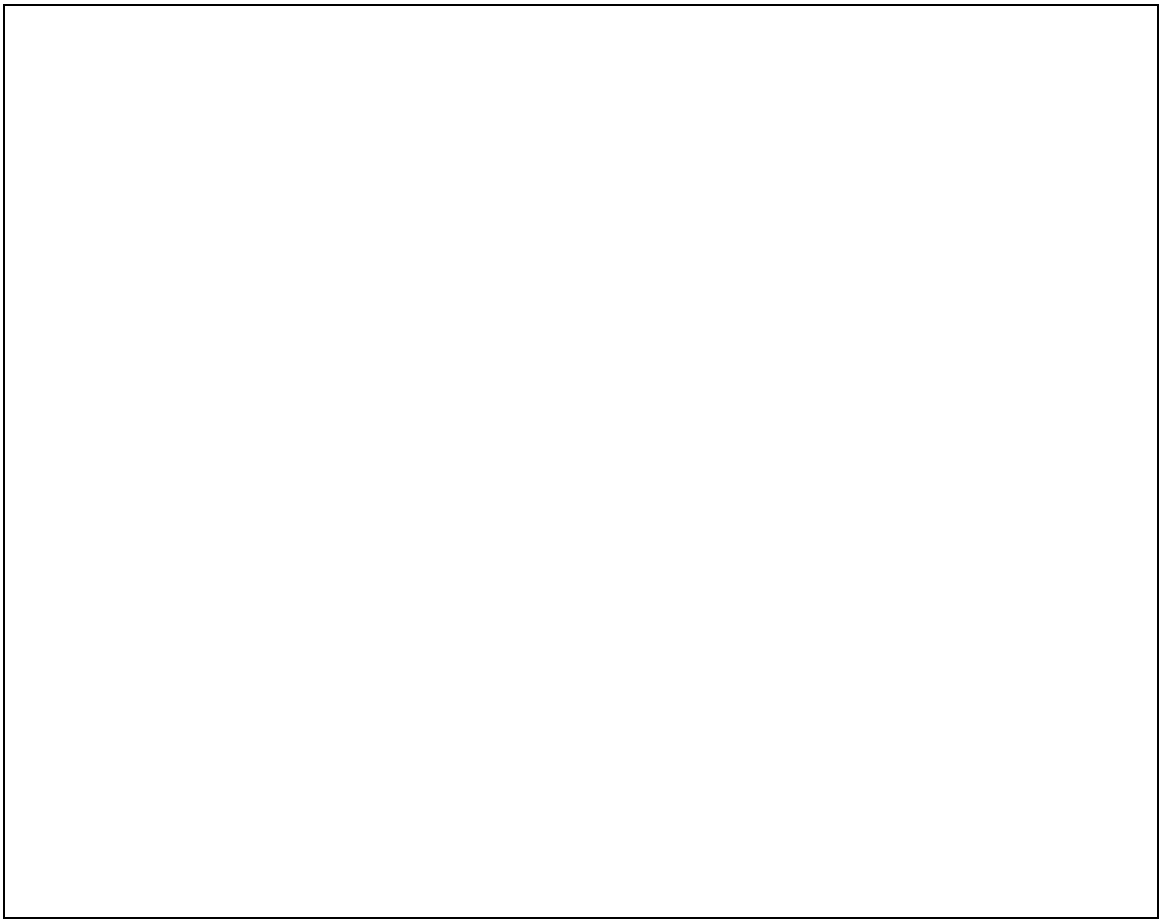
(b) Draw **two** chelation isomers of 2-(2-dimethylaminoethyl)phenyllithium. (6 p.)

chelation isomer 1
chelation isomer 2

(c) Are the chelated systems in **(a)** aggregated more or less than non-coordinating systems? State what Reich et al. found and state how they explained their findings. (8 points)

(d) Lithium comes as isotopes with masses 6 and 7. Which isotope is used in Li-NMR and why? Why is the other isotope not used? (10 points)

Isotope 1	Isotope 2	Isotope 3
Isotope	6Li	7Li
Natural abundance /%	7.59	92.41
Spin (I)	1	3/2
Frequency relative to 1H = 100 (MHz)	14.716086	38.863797
Receptivity, DP, relative to 1H = 1.00	0.000645	0.271
Receptivity, DC, relative to 13C = 1.00	3.79	1590
Magnetogyric ratio, g (107 rad T-1 s-1)	3.9371709	10.3977013
Magnetic moment, m (mN)	1.1625637	4.20407505
Nuclear quadrupole moment, Q (mbarn)	-0.808	-40.1
Line width factor, 1056l (m4)	0.033	21



Question 4. Effect of HMPA on the Reactivity of Epoxides. (25 points)

(a) Draw the lithiated derivatives of $(PhS)_2CH_2$ and of its all-*meta*-CF_3-substituted derivative. (6 points)

(b) Draw the product of the addition of $(PhS)_2CHLi$ to methyloxirane in THF at –78° C. (4 points)

(c) Schematically, draw a graphs that show the reaction rates (vertical) as a function of HMPA concentration (horizontal) for the reactions of both of the lithiated reagents of **(a)** with methyloxirane in THF at –78° C. (6 points)

(d) Provide a detailed reaction mechanism for the reaction in **(c)** and explain their different dependencies on [HMPA]. (9 points)