Structure Effects of Ion Pair Separation: Planar and Pyramidal Sulfur- and Silicon-Substituted Carbanions

Hans J. Reich* and Robert R. Dykstra

Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Received November 25, 1992

The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization, decreased inversion barriers at carbon, and increased charge delocalization to substituent groups. Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (o-phosphoryl, o-sulfinyl-, and o-sulfonylalkylthiiums) and lithium enolates coordinate through oxygen and not carbon and others are so delocalized (benzyldryl, trityl, fluorenyl, etc.) that C-Li association is weak. We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph2C1Li(TMEDA)7a and Ph2C1Li(12-crown-4).7b The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.46,3b,4c

We report the results of a low-temperature 13C, 7Li, 31P, and 29Si NMR study of the sulfur- and silicon-substituted organolithium reagents 1-4 in which we show that ion separation may give either planar or pyramidal carbanions. We will abbreviate Li-SiPh2 and Li-SiPh2 as contact ions and Li-SiPh2 and Li-SiPh2 as separate ion pairs. We will use the symbol / to indicate separated ions (Scheme I).

The 7Li, 31P, and 29Si NMR spectra of 13C-enriched compound. Above 2 equiv of THF/HMPA can be reliably determined by NMR spectroscopy have made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

The discovery7a,7b,10 that solvation and ion pair status of many lithium reagents in THF/HMPA may be determined by NMR spectroscopy has made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization, decreased inversion barriers at carbon, and increased charge delocalization to substituent groups. Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (o-phosphoryl, o-sulfinyl-, and o-sulfonylalkylthiiums) and lithium enolates coordinate through oxygen and not carbon and others are so delocalized (benzyldryl, trityl, fluorenyl, etc.) that C-Li association is weak. We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph2C1Li(TMEDA)7a and Ph2C1Li(12-crown-4)7b. The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.46,3b,4c

The discovery7a,7b,10 that solvation and ion pair status of many lithium reagents in THF/HMPA may be determined by NMR spectroscopy has made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization, decreased inversion barriers at carbon, and increased charge delocalization to substituent groups. Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (o-phosphoryl, o-sulfinyl-, and o-sulfonylalkylthiiums) and lithium enolates coordinate through oxygen and not carbon and others are so delocalized (benzyldryl, trityl, fluorenyl, etc.) that C-Li association is weak. We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph2C1Li(TMEDA)7a and Ph2C1Li(12-crown-4)7b. The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.46,3b,4c

The discovery7a,7b,10 that solvation and ion pair status of many lithium reagents in THF/HMPA may be determined by NMR spectroscopy has made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization, decreased inversion barriers at carbon, and increased charge delocalization to substituent groups. Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (o-phosphoryl, o-sulfinyl-, and o-sulfonylalkylthiiums) and lithium enolates coordinate through oxygen and not carbon and others are so delocalized (benzyldryl, trityl, fluorenyl, etc.) that C-Li association is weak. We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph2C1Li(TMEDA)7a and Ph2C1Li(12-crown-4)7b. The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.46,3b,4c

The discovery7a,7b,10 that solvation and ion pair status of many lithium reagents in THF/HMPA may be determined by NMR spectroscopy has made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization, decreased inversion barriers at carbon, and increased charge delocalization to substituent groups. Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (o-phosphoryl, o-sulfinyl-, and o-sulfonylalkylthiiums) and lithium enolates coordinate through oxygen and not carbon and others are so delocalized (benzyldryl, trityl, fluorenyl, etc.) that C-Li association is weak. We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph2C1Li(TMEDA)7a and Ph2C1Li(12-crown-4)7b. The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.46,3b,4c

The discovery7a,7b,10 that solvation and ion pair status of many lithium reagents in THF/HMPA may be determined by NMR spectroscopy has made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization, decreased inversion barriers at carbon, and increased charge delocalization to substituent groups. Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (o-phosphoryl, o-sulfinyl-, and o-sulfonylalkylthiiums) and lithium enolates coordinate through oxygen and not carbon and others are so delocalized (benzyldryl, trityl, fluorenyl, etc.) that C-Li association is weak. We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph2C1Li(TMEDA)7a and Ph2C1Li(12-crown-4)7b. The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.46,3b,4c

The discovery7a,7b,10 that solvation and ion pair status of many lithium reagents in THF/HMPA may be determined by NMR spectroscopy has made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization, decreased inversion barriers at carbon, and increased charge delocalization to substituent groups. Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (o-phosphoryl, o-sulfinyl-, and o-sulfonylalkylthiiums) and lithium enolates coordinate through oxygen and not carbon and others are so delocalized (benzyldryl, trityl, fluorenyl, etc.) that C-Li association is weak. We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph2C1Li(TMEDA)7a and Ph2C1Li(12-crown-4)7b. The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.46,3b,4c

The discovery7a,7b,10 that solvation and ion pair status of many lithium reagents in THF/HMPA may...
downfield shifts for the ipso and upfield shifts for the para carbons between C–H and C–Li. In compounds 1-Li to 4-Li, the charge is not directly conjugated with the benzene ring, and the small upfield para shifts reflect a correspondingly small degree of charge polarization. We feel that the large ipso shifts cannot be solely due to charge polarization and propose that they are a consequence of $n \rightarrow \sigma^*$ hyperconjugative interactions ($R_2C-S-Ph \leftrightarrow R_2C=S-Ph$). Such interactions represent an important carbanion-stabilizing mechanism.

The ring quaternary carbons C-4 and C-5 of 1 shift downfield, just as do related carbons in 3 on going from C–H to contact C–Li. However, an upfield shift of these carbons was observed on going to the solvent-separated species 1/HLi* (Figure 2D). We interpret this upfield shift in terms of a reduction of hyperconjugative interaction into the ring. The Si-Ph groups show significantly higher than normal ipso carbon downfield and para carbon upfield shifts on ion separation, and this may suggest an increase in the interaction of the carbanion center within the exocyclic silyl phenyls.

The divergent behavior of 1 and 2 can be rationalized by considering two limiting structures. The first has a pyramidal carbon and a puckered ring and planar carbanion places the lone pair orthogonal to the CS bonds, and in a position to interact in a destabilizing fashion with sulfur lone pairs.

Acknowledgment. We thank the National Science Foundation for support of this work.

Supplementary Material Available: $^{13}$C chemical shifts and coupling constants for PhS(PhSe)CHLi, (PhSe)$_2$CHLi, PhS-(PhMe$_2$Si)CHLi, PhSe(PhMe$_2$Si)CHLi, and Ph(PhSe)CHLi; HMPA titration of 2 (2 pages). Ordering information is given on any current masthead page.


(15) The $^1$H-carbon of PhLi is strongly downfield shifted; Jones, A. J.; Grant, D. M.; Russell, J. G.; Franzen, G. J. Phys. Chem. 1969, 73, 1624.