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Solution Structure of Allenyl−Propargyllithium Reagents[1]

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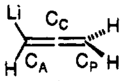
In spite of substantial use of allenyl−propargyllithium reagents in synthetic chemistry[2] as well as spectroscopic[1a,3−7] and theoretical[8] studies of their structures, the allenyl−propargyl nature (**1**, **2**) of most such reagents has not been established.[9] We report here preliminary results of an NMR spectroscopic study which addresses the allenyl−propargyl dichotomy and the extent of aggregation.



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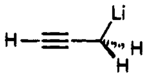

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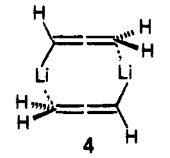

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The IR[3] and ^{13}C NMR[4a] spectra of the metalation product of allene have been interpreted in terms of an allenyllithium structure. We have reexamined allenyllithium in THF at low temperature and have detected two species, whose ratio is concentration dependent. Both are clearly allenic in structure, on the basis of the downfield shift of the central carbon C_C, near 190 ppm (the central carbon of allene appears at 213 ppm), the propargyl terminus C_P (44 ppm), and the well-defined ^{13}C−^{7}Li coupling of the allenyl carbon C_A (88 ppm, Figure 1). The 1:1:1:1 quartet identifies the species favored at lower concentration as the monomer **1**.[10] The 1:2:3:4:3:2:1 septet suggests a 4-centered cyclic dimer **3** with C_A coupled equally to two ^{7}Li nuclei.[11] Thus, allenyllithium dimerizes in the normal fashion of most localized organolithium reagents; head-to-tail dimers such as **4** are not detectably present.[12]

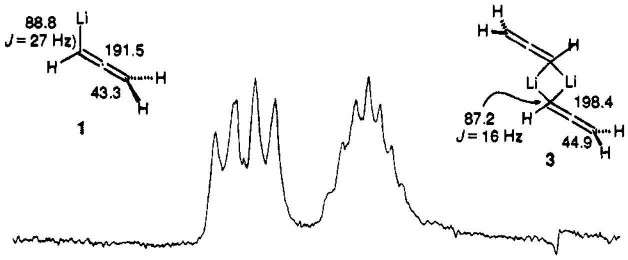
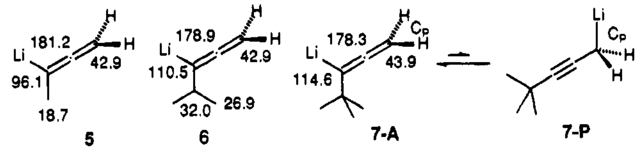


Figure 1. ^{13}C NMR spectrum (90.56 MHz) of C-1 of allenyllithium, −150 °C in 2.5:1:1 Me_2O/THF/pentane.

Alkyl substitution at the carbanionic carbon generally destabilizes organolithium reagents, and indeed, the metalation products of 2-butyne (**5**)[7] and 4-methyl-2-pentyne (**6**)[6] are reported to have the propargyllithium or equilibrating allenyl−propargyl structures. We have also reexamined **5** and **6**, as well as the *tert*-butyl analog **7** not previously reported, and have found them to be monomeric allenyllithium structures in THF on the basis of ^{13}C chemical shifts and ^{13}C−^{7}Li couplings analogous to those of allenyllithium itself.



5 **6** **7-A** **7-P**

^{13}C Chemical Shifts at -140 to -145° C

We have estimated the fraction of the propargyllithium isomer present for **7**, selected because the *tert*-butyl substituent at C_A should maximally destabilize the allenyl structure. Since the equilibration between **7-A** and **7-P** must be intramolecular (J_{C-Li} coupling), the propargyl carbon C_P would be broadened by C−Li coupling in proportion to the fraction of **7-P** present. The line width of C_P (3.5 Hz) is only 1.2 Hz greater than that of the central carbon C_C, thus J_{C-Li} for the propargyl carbon is <0.4 Hz ($J = {}^{1}/_{3}\, \nu_{1/2}$). If we estimate that the full J_{C-Li} for **7-P** is 16 Hz (see below for data on some authentic propargyllithium reagents), the line width of the fully coupled C_P carbon would be >48 Hz (3*J*), and there could be no more than 3% of propargyllithium isomer **7-P** present. Related compounds with methyl, propyl, isopropyl, butyl, and *tert*-butyl substituents at C_A and C_P were also monomeric in THF and had the allenyl structure.

Does this mean that there are no propargyllithium reagents? The metalation product of dicyclopropylacetylene has been reported to have structure **8-P** on the basis of its IR spectrum.[13] We have reexamined this lithium reagent by ^{13}C NMR and can confirm this conclusion. The central carbon C_C is now at 99.9 ppm, compared to ≈180 ppm for **1**, **5**, **6**, and **7**, and C_P at −7.5 ppm, instead of at 43 ppm. Thus the increase in ring strain for **8-A** on going from formally an sp^3 to an sp^2 cyclopropyl carbon[14] is sufficient to overwhelm the normal preference for an allenyllithium structure. Several arylated propargyllithium

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[10] Monomeric organolithium reagents are commonly observed in THF.[1d] Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371. Seebach, D.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1984**, *67*, 1083.

[11] Accurate measurements of the concentration dependence of the monomer to dimer ratio were hampered by the formation and precipitation of 1-lithiopropyne. Allyllithiums show no sign of Li−C coupling.[9a]

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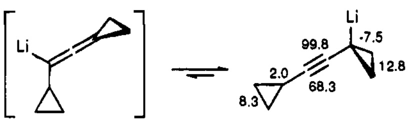
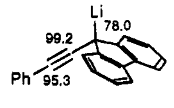
reagents (e.g., **9**) have been identified by ^{13}C NMR and single-crystal X-ray spectroscopy, although these are reported to be largely solvent-separated delocalized ion pairs in THF.[5]

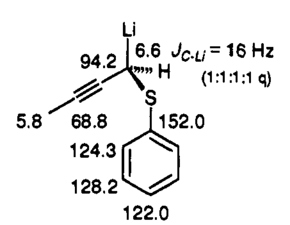


8-A **8-P** (δ ^{13}C, Me$_2$O, -35 °C)

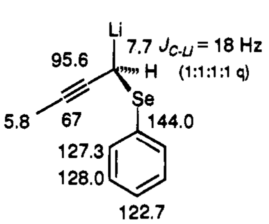


9 (THF, -78 °C)

Examination of the lithium reagent **10**, prepared by metalation of 1-(phenylthio)-2-butyne, showed that it also has a propargyl structure. The central carbon C$_C$ is at 94.2 ppm, and the signal for C$_P$ at 6.6 ppm now showed ^{13}C$-^7$Li coupling (instead of C$_A$ at 90−120 ppm for **1**, **5**, **6**, and **7**). Similar line width considerations as discussed for **7** indicated that <1% of allenyllithium could be present. The phenylseleno analog **11**[1b] is also propargylic.



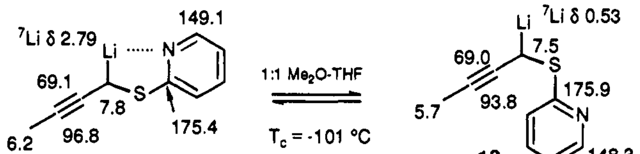
10 (-145 °C)



11 (-120 °C)

^{13}C Chemical Shifts

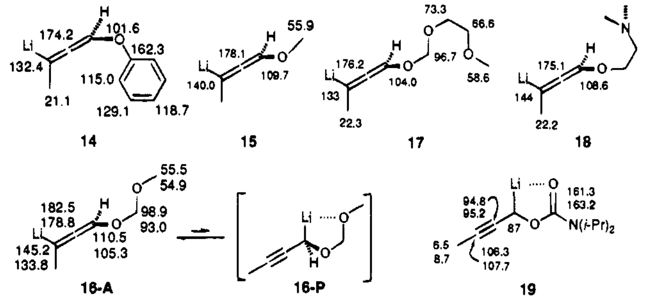
The replacement of phenyl by 2-pyridyl significantly changes the chemistry of sulfur-substituted allyllithium reagents,[15] effects ascribed to N-chelation. We have examined the 2-pyridyl analog of **10**, compound **12**. This is also a propargyllithium reagent, but a 3:2 ratio of two species was observed in THF solution. The two signals coalesced near −100 °C, and their ratio was concentration independent (0.01−0.18 M). The minor isomer disappeared in the poorer donor solvent 2,5-dimethyltetrahydrofuran. The two species had very similar ^{13}C NMR spectra, but there was a large difference in the lithium chemical shifts, 0.53 ppm for the minor and 2.79 ppm for the major isomer (0.3 M LiCl/MeOH reference). The solvent dependence of the isomer ratio and the Li shifts provide the best support for the assignment of these peaks to the chelated (**12**) and nonchelated (**13**) rotamers at the C−S bond. Coordination of pyridine to lithium causes substantial downfield shifts,[16] as observed for the major isomer. High rotation barriers have been detected in several phenylthio- and phenylseleno-substituted alkyllithium reagents.[1c,17]



12 **13**

Chemical Shifts at -130 °C in 1:1 THF/Me$_2$O

Allenyl−propargyllithium reagents with oxygen substituents (alkoxy, carbamoyloxy) are useful reagents for C−C bond formation.[1e,18] (1-Methoxyallenyl)lithium, with substitution at C$_A$, is allenic in nature and dimeric in THF.[8b] We have examined several reagents (**14**−**18**) which have oxygen substituents at C$_P$ to determine whether these, like the sulfur and selenium groups discussed above, favor the propargyl isomer (possible coordination between lithium and the ether oxygens).[5b,19] Not only the metalation product of 1-phenoxy-2-butyne (**14**) and 1-methoxy-2-butyne (**15**) but even the MOM (**16**), MEM (**17**), and β-(dimethylamino)ethoxy (**18**) analogs, with intramolecular 5- and 6-ring chelation possible in a propargyl structure, are allenyllithium reagents. Either the chelation fails to compete with coordination by solvent (THF or Me$_2$O) or the inherent thermodynamic preference for allenyllithium is larger than any stabilization provided by chelation.[20] MOM-substituted compound **16** showed doubled signals in the ^{13}C NMR spectrum in THF; in ether only a single set of resonances was observed. The origin of the signal doubling is not known. Dimeric diastereomers or different aggregates (as for **1**) are possibilities.



14 **15** **17** **18** **16-A** **16-P** **19**

^{13}C Chemical Shifts in THF-ether at -110 to -130 °C

Hoppe and co-workers have developed synthetic applications of a series of carbamoyloxy-substituted alkyl, allyl, and allenyllithium reagents, including several chiral nonracemic ones.[18a] We have examined compound **19**. As can be seen from the ^{13}C NMR chemical shifts, the compound is unambiguously propargylic. In THF all signals (^{13}C, ^{7}Li, ^{6}Li) were doubled; in ether four sets of signals were observed. Well-resolved C−Li couplings were not detected for either ^{7}Li or ^{6}Li, although the peak shape of C$_P$ in THF strongly suggested coupling to a single lithium. The ratio of peaks remained 1:1 from 0.04 to 0.32 M, and the two species coalesced near −72 °C. We suggest diastereomeric O-bonded dimers for the two species in THF.

We have shown here that allenyl−propargyllithium reagents have an inherent bias toward allenyllithium structures. Neither alkyl groups on the allenyl carbon nor ether groups on the propargyl carbon favor the propargyl isomer sufficiently for it to be detected. Even reagents with ether substituents in a position to stabilize the propargyl isomer by lithium chelation are unambiguously allenic. However, three types of reagents do have a propargyl structure: those with two substituents at the propargyl carbon forming a cyclopropane ring (I-strain), those with good carbanion stabilizing groups such as Ph,[5] PhS, or PhSe at the propargyl carbon, and those in which a powerful chelating group, such as carbamoyl, stabilizes the propargyl structure.

Acknowledgment. We thank the National Science Foundation for support of this work and Gwynne M. Wesley for the preparation of dicyclopropylacetylene.

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