

corresponding to an allyltitanium species,^[21] the results indicate that transmetalation is not occurring and that the complex functions as a Lewis acid.

The new catalytic, enantioselective addition of allyltrimethylsilane to aldehydes described here is thus an alternative to methods that employ organotin reagents. The success of the reaction is attributed to the unique reactivity of a fluorotitanium complex prepared in acetonitrile from TiF_4 and (*R*)- or (*S*)-1,1'-bi-2-naphthol. The additions with allyltrimethylsilane are possible with the discovery that the TiF_4 -derived catalyst is more reactive than the chloro-, bromo-, and alkoxytitanium complexes that have been previously employed. These results present new opportunities for the design and synthesis of well-defined chiral fluorotitanium complexes as catalysts in a variety of other important stereoselective processes. The study of such optically active complexes and their subsequent application are currently under investigation in our laboratory and will be reported in due course.

Experimental Procedure

To a solution of (*S*)-(-)-1,1'-bi-2-naphthol (57 mg, 0.20 mmol) in MeCN (0.5 mL) was added TiF_4 (0.20 mL, 0.10 mmol; 0.5 M solution in MeCN) to give a deep red solution that was stirred for 5 min prior to removing the solvent under reduced pressure. The residue was kept under reduced pressure (1 mm Hg) for 0.5 h and subsequently suspended in CH_2Cl_2 (0.5 mL), cooled to 0 °C, and treated dropwise with allyltrimethylsilane (0.24 mL, 1.5 mmol). After the mixture had been stirred at 0 °C for 1.5 h, the resulting red orange solution was treated with 2,2-dimethyl-4-pentenol (0.14 mL, 1.0 mmol). The reaction mixture was stirred at 0 °C for 4 h and then diluted with Et_2O /pentane (1:2; 10 mL). The mixture was filtered through a plug of silica and the filter cake washed with Et_2O /pentane (1:2; 50 mL). The filtrate was concentrated in vacuo to an oil, which was diluted with THF (2.0 mL). The resulting solution was treated with Bu_4NF (1.0 mL of a 1.0 M solution in THF), and stirred at 23 °C for 0.5 h. The reaction was quenched with Et_2O (50 mL) and washed with H_2O (20 mL). The ether extract was washed with saturated aqueous sodium chloride solution, dried over anhydrous Na_2SO_4 , and concentrated in vacuo to give a colorless oil. Purification by chromatography on silica gel with Et_2O /pentane (1/10) afforded 138 mg (90%) of the product.

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- [6] As part of some very elegant work on Ti-carbohydrate complexes in organic synthesis, Hafner and Duthaler have reported that the addition of the allyltitanium reagent $\text{CH}_3\text{Ti}(\text{O}i\text{Pr})_3$ to aldehydes is catalyzed by CpTiF₄ (TADDOLate), (TADDOL = $\alpha\alpha'\alpha''$ -tetraaryl-2,2-dimethyl-1,3-dioxolan-4,5-dimethanol): A. Hafner, R. O. Duthaler *Abstr. Pap. Seventh IUPAC Symposium on Organo-Metallic Chemistry Directed Towards Organic Synthesis (OMCOS-7)*, Kobe, Japan, 22.
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Structure of Silyl-Substituted Allenyl/Propargyllithium Reagents in Solution**

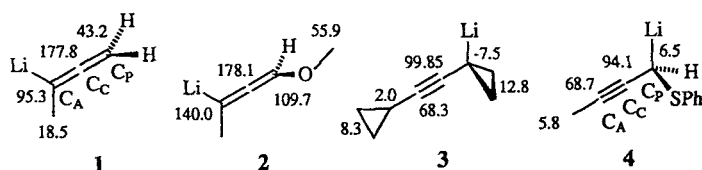
Hans J. Reich* and Johnathan E. Holladay

Theoretical studies of $\text{C}_3\text{H}_3\text{Li}$, which could formally be either allenyl- or propargyllithium, have predicted a primarily allenyl structure.^[1, 2] Experimentally, the question of structure has been addressed by X-Ray crystallography,^[2, 3] IR spectroscopy,^[1a, 4, 5] and ^{13}C NMR spectroscopy.^[6a, b, 1a, 7] Both the central carbon (C_c , $\delta = 165\text{--}180$ for allenyl, $\delta = 90\text{--}100$ for propargyl) and the propargyl carbon (C_p) are very sensitive indicators of structure. Most reagents investigated have an allenyl structure; this includes compounds with alkyl groups at C_α (for example 1 and 2, Scheme 1),^[6a, b] which might destabilize the allenyl isomer. A few well-defined propargyllithium reagents are known in which C_p bears either a strained ring (3),^[5, 6b] one or two carbanion stabilizing groups (PhS (4),^[6b] PhSe ,^[6b] Ph ^[2, 7]), or a strong chelating group (carbamoyloxy).^[6b, 8] We report results of an NMR study of silyl-substituted allenyl/propargyllithium reagents,^[9] which provide insight into the thermodynamics, kinetics, and stereochemistry of the allenyl/propargyllithium interconversion, as well as the effect of lithium coordination on the electronic structure.

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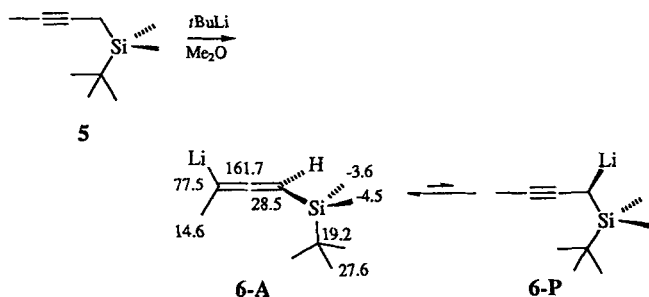
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Scheme 1. ^{13}C chemical shifts of 1–4 in THF and Me_2O

The chemical shifts of the lithium reagent **6** (prepared by metalation of the propargylsilane **5**, Scheme 2) in THF are unambiguously allenic and essentially temperature-independent. Well-defined ^{13}C – ^7Li coupling to C_A ($\delta = 77.5$, q (1:1:1:1), $J = 21$ Hz at -152°C) and none to C_P is observed, indicating



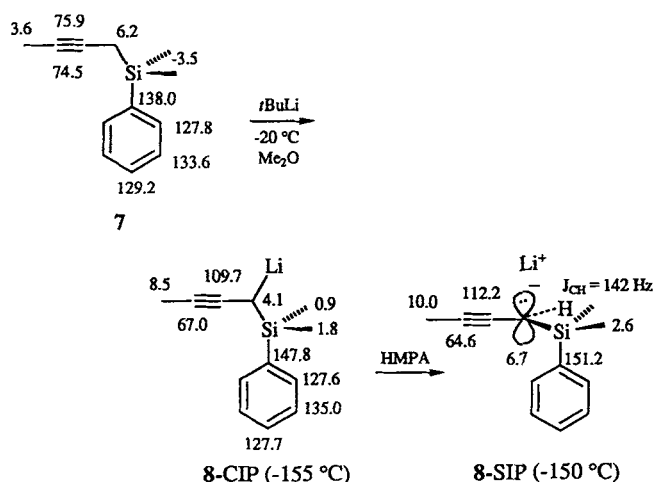
Scheme 2. Preparation and ^{13}C chemical shifts ($T = -152^\circ\text{C}$) of 6-A.

the monomeric nature of the compound and localized bonding to lithium. At -135°C the maximum broadening for C_P is 2 Hz more than for C_A and C_C . Thus, $J_{\text{C-Li}}$ for C_P is less than 0.6 Hz. Assuming that this value for a propargyl isomer is at least 15 Hz, there can be no more than 4% of **6-P** present. Values of 16 and 18 Hz have been measured for C_P ^7Li – ^{13}C couplings in **4** and its selenium analog.^[6b]

Because of the chiral allenyl group, the SiMe_2 group of **6** is diastereotopic at low temperature. The racemization of **6** can be detected by coalescence of the signals for the SiMe_2 group (coalescence temperature -135°C , $\Delta G^\ddagger_{-142^\circ\text{C}} = 6.3$ kcal mol^{-1}). A remarkable feature of the racemization is that it is intramolecular;^[10] the Li – C_A coupling persists to more than 20°C above the coalescence temperature ($\Delta\delta = 81$ Hz between the diastereotopic Me groups).^[11] A barrier to inversion could also be estimated for **8** ($k = 400$ sec^{-1} at -137°C , $\Delta G^\ddagger = 6.1$ kcal mol^{-1}).

The ^{13}C NMR spectra of **8** (generated from **7**, Scheme 3), the phenyl analog of **6**, are less clear-cut. The strongly temperature-dependent chemical shift values are between those expected for allenyl and propargyl isomers, and the signals show poorly resolved Li – C coupling. The propargyl-like C_C shifts at low temperature move progressively towards allenyl values at higher temperatures. Since variations in chemical shifts of over 30 ppm (between -155 and -35°C) are unlikely to arise from altered conformer populations or extent of solvation, substantial changes in structure or equilibrium composition must occur.

Figure 1 shows chemical shifts of C_C for a range of lithium reagents, from those that appear to be allenic (such as **1**) to those that are unambiguously propargylic (such as **4**). Compounds with intermediate δ values (**8**–**11**) must either consist of significant fractions of both allylic and propargyl isomers in rapid equilibrium on the NMR time scale or have a 1,3-lithium-bridged structure such as **12** in which the asymmetry of bridging is temperature-dependent. Such bridged structures have been



Scheme 3. Preparation and ^{13}C chemical shifts of **8** in Me_2O (CIP) and Me_2O –HMPA (SIP). See text for further details.

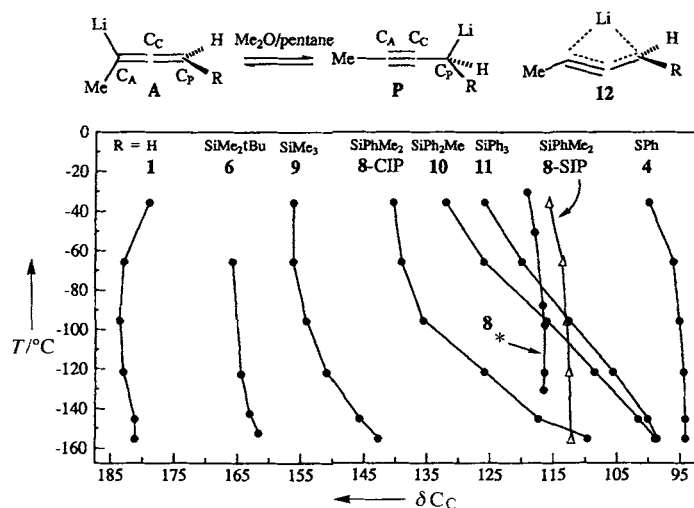


Fig. 1. Temperature dependence of the central carbon ^{13}C NMR chemical shifts of allenyl/propargyllithium reagents in THF/ Me_2O (* = in 2,5-dimethyltetrahydrofuran).

predicted by calculations of unsolvated allenyllithium species, and there is evidence from HOESY experiments that dimeric 1-methoxyallenyllithium is partially bridged.^[1a, 1b, 12] Since two species are detected by IR spectroscopy, we prefer an explanation involving tautomeric structures (although both could be unsymmetrically bridged). Absorptions at 1894 (strong) and 2179 (medium) cm^{-1} for **8** at -78°C indicate the presence of both allenyl and acetylenic structures.^[1a, 4, 5] In contrast, the 2-pyridyl analog of **4** shows only an acetylenic stretch at 2164 cm^{-1} , whereas **1** shows an absorption at 1885 cm^{-1} . The ^{13}C chemical shifts of **1** and **4** are not significantly temperature-dependent; a static bridged structure such as **12** should not show the large changes in shift observed for **8**–**11**. If our interpretation of two tautomeric structures is correct, the propargyl isomer is enthalpically favored, whereas the allenyl isomer is entropically favored ($\Delta H^\circ = 1.1 \pm 0.2$ kcal mol^{-1} , $\Delta S^\circ = 6.1 \pm 1$ eu for **8**).^[13] Solvation must play a key role in the structural changes, since the C_C chemical shifts of **8** in 2,5-dimethyltetrahydrofuran are only slightly temperature-dependent ($\delta = 119.2$ at -30°C , 116.6 at -130°C , Fig. 1).^[14]

The temperature dependence and solvent effect suggest a difference in solvation between the allenyl and propargyl species.

Perhaps the more highly directional, formally sp^2 -hybridized carbanion orbital at the allenyl carbon C_A strengthens C–Li bonding and reduces the level of lithium solvation relative to that of the formally sp^3 -hybridized propargyl carbanion carbon C_P . Higher temperatures would favor the isomer with the lower degree of solvation. Stronger C–Li covalency at C_A would also explain the tendency for more allenyl character in the contact ion pairs than in the solvent-separated ion pairs, as seen in most of the systems studied (see below).

When methyl groups on silicon are replaced by the more electron-withdrawing phenyl groups (compare **9** with **8**, **10**, and **11**), the fraction of propargyl isomer increases. This is consistent with the general observation that carbanion stabilizing groups (such as Ph, PhS, PhSe, or R_3Si) at the propargyl carbon favor the propargyl isomer. On the other hand, substitution of the methyl group on silicon by a *tert*-butyl group results in **6**, which has predominantly or exclusively allenyl character.

The identification of lithium reagents that are equilibrating mixtures of allenyl and propargyl isomers allowed an estimation of their rate of interconversion from DNMR line broadening. We chose the Me_3Si reagent **9** for more careful study, since it has nearly equal amounts of the two isomers at the lowest temperature investigated (Fig. 1). At $-150^\circ C$ in $Me_2O/Et_2O/THF$ (5/2/1) the signal for C_C of **9** (estimated shifts of $\delta = 165$ and 98 in the two isomers) is 17 Hz wide. This gives a rate constant k greater than 10^5 sec^{-1} and a free energy of activation ΔG^\ddagger smaller than 4 kcal mol^{-1} for interconversion of the isomers **9-A** and **9-P**. This low barrier to 1,3-lithium shift^[15] has implications for the role of the isomeric lithium structures in the regioselectivity of reactions. Unless the rate of reaction for a lithium reagent with a substrate is greater than the rate of interconversion, the isomeric nature of the lithium reagent will not directly control the isomer produced (Curtin–Hammett principle). The rates of reaction for allenyl/propargyllithium reagents with typical substrates in THF are unknown. The very low barrier established here implies that the ratio of isomeric structures will directly determine regioselectivities for only the most rapid, if any, reactions of allenyl/propargyllithium reagents (ΔG_{-85}^\ddagger for the reaction of $nBuLi$ dimer and tetramer with benzaldehyde is about $9\text{--}10 \text{ kcal mol}^{-1}$ ^[16]). The controlling feature will be the inherent reactivity of the individual isomers weighted by their concentrations. This conclusion is consistent with observations that a single allenyl/propargyllithium reagent can give dramatically different ratios of products with different electrophiles.^[6c, 17]

HMPA titrations^[6c] were carried out on most of the lithium reagents to establish the effect of lithium coordination on structure. Addition of HMPA to **8** first forms a mono-HMPA contact ion pair (CIP) followed by ion pair separation. Formation of the separated ion pair (SIP) is complete with four equivalents of HMPA. The chemical shifts are essentially temperature-independent (Fig. 1) and more propargyl- than allenyl-like. Although the C_C chemical shifts vary over 65 ppm (99 to 165 ppm) in the CIPs of **8** to **11**, the range for the SIPs is narrower (from $\delta = 106.9$ for $SiPh_3$ to $\delta = 118.7$ for $SiMe_2tBu$, $\delta(C_P)$ varies by only 2 ppm). The one-bond C–H coupling is significantly larger in the SIP (for example 146 Hz, for the $SiPh_3$ compound **11**) than in the CIP (128 Hz). Thus, there appears to be significant planarization of the carbanion carbon^[6d] upon ion separation, but it is accompanied by surprisingly little change in the chemical shifts.

The significant changes in the ratio of propargyl to allenyl isomers that occur in compounds **8–11** can be principally ascribed to details of the interaction of the lithium cation and its

associated solvent molecules with the anion. Changes in the inherent electronic structure of the carbanion play only a minor role.

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