Lithium Metalloid Exchange:[1] Reactivity Studies of an Allenyllithium Reagent using an Isomeric Pair of Allenyl and Prop-2-ynyl Stannanes

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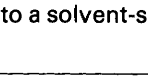
The regioselectivity and reactivity of silylation of an allenyl–prop-2-ynyllithium reagent is different when a sequential or *in situ* Li/Sn exchange is used to prepare it; the evidence points to a solvent-separated ion pair as the transient species trapped during the *in situ* experiment.

Allenyl–prop-2-ynyllithium reagents have been studied experimentally[2] and theoretically,[3] yet no consistent rationale for regioselectivity has emerged. We report lithium–tin exchange studies of isomeric stannanes **1A** and **1P**† whose goal was to probe the origins of allenyl–prop-2-ynyl selectivity and the possible role of tin 'ate' complexes in the chemistry of these allenyllithium reagents.[1a]

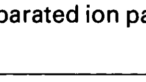
Two types of experiments were performed. In the first (sequential), methyllithium was added to the tin compound, followed by Me_3SiCl about 10 s later. A 2/98 ratio of allenyl to prop-2-ynyl silane (**2A/2P**) was seen independent of concentration, order of addition (lithium reagent to silyl chloride, or the reverse), equivalents of Me_3SiCl, or starting stannane (Table 1). In the second type (*in situ*), methyllithium was added to a mixture of tin compound and electrophile.‡ Highly variable amounts of allenyl silane **2A** were formed under these conditions. At least two reactive species must be undergoing silylation. A transient intermediate, species T, is formed first and gives predominantly **2A** on reaction with Me_3SiCl. It converts quickly (<10 s) to stable species S, which forms almost exclusively **2P**. The increase in the ratio **2A/2P** as the concentration of Me_3SiCl was increased [Fig. 1(*a*)–(*g*)] results from more efficient trapping of species T in competition with its conversion to species S.

We assign an allenyllithium structure to the equilibrium lithium reagent (perhaps species S) from its ^{13}C NMR spectrum (Fig. 2). The methyls of the isopropyl group were disastereotopic up to −60 °C because of the chiral allene unit [$\Delta G^\ddagger > 12$ kcal mol^{-1} (1 cal = 4.184 J) for racemization].[4]

We do not feel that two aggregation states, *e.g.* species T a monomer, S a dimer, explain our results. First, the lithium reagent is monomeric in 1/1 tetrahydrofuran (THF)–diethyl ether, as shown by the 25 Hz 1:1:1:1 quartet for C-4 (δ 117.6) due to ^7Li–^{13}C coupling. Second, even if there was some weak head-to-tail dimer association not detectable by C–Li coupling, such association would be reduced in THF–HMPA (hexamethylphosphoramide). Yet the difference between *in situ* and sequential experiments became larger



A



P

1; M = Me_3Sn
2; M = Me_3Si
3; M = Me_2Pr^iSi
4; M = Me_2PhSn
5; M = $MePh_2Sn$
6; M = Ph_3Sn
7; M = Li
8; M = Me_3RSn^-

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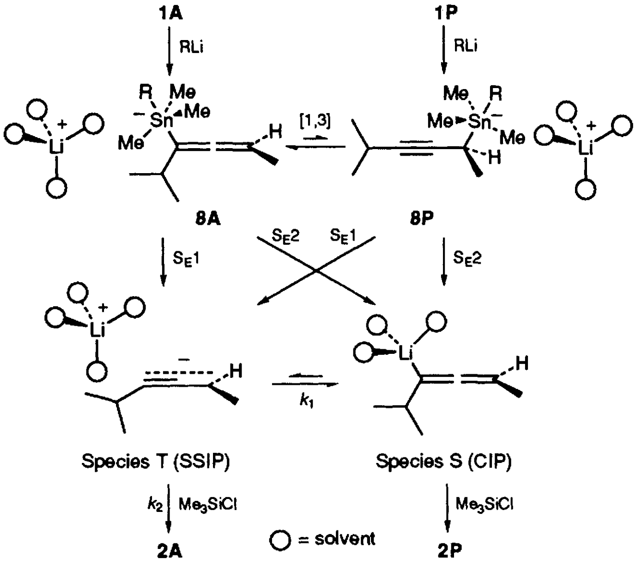
† These compounds were prepared as follows: 3-methylbut-1-yne was converted to 5-methyl-2-methylselenohex-3-yne (Bu^nLi, MeCHO; $MeSO_2Cl$, NEt_3; MeSeLi). Li/Se exchange and stannylation gave **1P** under kinetic control (MeLi, 0 °C; $MgBr_2$; 1.1 Me_3SnBr) and **1A** under thermodynamic control (MeLi, 0 °C; 0.95 Me_3SnBr).

‡ Trapping experiments were carried out at −78 °C in THF, 0.067 mol dm^{-3} tin compound, with halide free RLi (1.2 equiv.) and silyl chloride (3 or more equiv.). Analysis was by calibrated capillary GC. Typical recoveries were >80%, conversions varied from 25 to 100%, depending on the experiment.

Table 1. Product ratios from reaction of allenyl and propynyl stannanes with Me_3SiCl

				2A/2P Starting from:			
				A	P	A	P
Entry	M	RL	Solvent	*In situ*		Sequential	
1	Me_3Sn	MeLi	THF	39/61	14/86	2/98	2/98
2	Me_3Sn	MeLi	THF–2HMPA	81/19	79/21	5/95	4/96
3	Me_3Sn	PhLi	THF	27/73	28/72	2/98	2/98
4	Me_2PhSn	MeLi	THF	30/70	26/74	2/98	2/98
5	Me_2PhSn	PhLi	THF	7/93	8/92	2/98	2/98
6	Me_2PhSn	MeLi	THF	10/90	9/91	2/98	2/98
7	$MePh_2Sn$	PhLi	THF	4/96		2/98	2/98
8	Ph_3Sn	MeLi	THF	2/98	3/97	2/98	2/98



Scheme 1

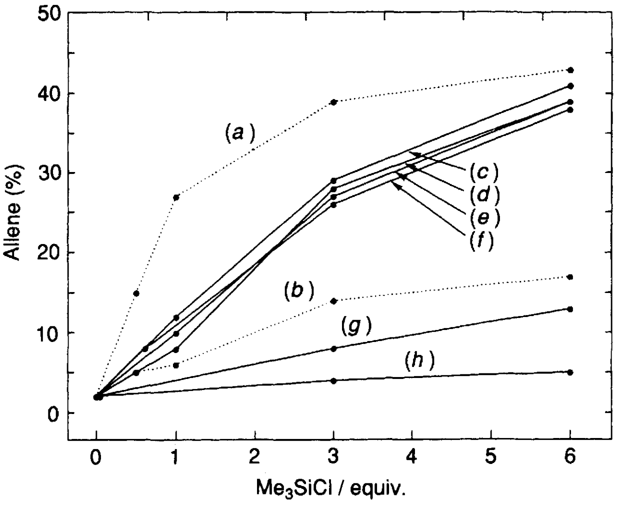


Fig. 1 Relative yield of **2A** and **2P** as a function of [Me_3SiCl] (THF at −78 °C, *in situ* experiment): (*a*) **1A** + MeLi, (*b*) **1P** + MeLi, (*c*) **4A** + MeLi, (*d*) **1P** + PhLi, (*e*) **1A** + PhLi, (*f*) **4P** + MeLi, (*g*) **5P** + MeLi and (*h*) **5P** + PhLi

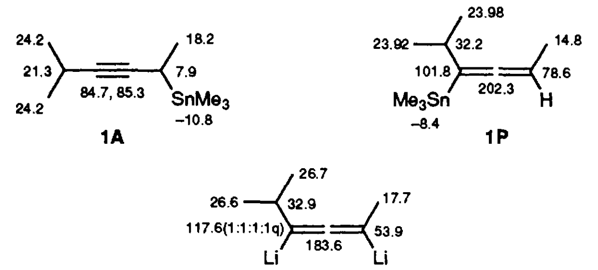


Fig. 2 ^{13}C NMR data (δ) for **1A**, **1P** and **7A**

under these conditions (*in situ*: **2A**/**2P** 81/19; sequential: 5/95; Table 1 entries 1 and 2).

Additional characterization of species S and T was provided by competitive double trap experiments, in which a mixture of two electrophiles, Me_3SiCl and Pr^iMe_2SiCl, was used. In THF both sequential and *in situ* experiments using methyllithium or phenyllithium on **1A** or **1P** gave prop-2-ynyl products **2P** and **3P** in a 91/9 ratio. We therefore conclude that even in the *in situ* experiments, the prop-2-ynyl product comes from species S, and species T gives only allenyl products. In the *in situ* experiments, species T gave **2A** and **3A** with a low selectivity (60/40 or less), implying that it is much more reactive, and hence less selective than species S.

The 'ate' complex intermediate in the Li/Sn exchange[1a,b] must play a role in the reaction, since *in situ* allenyl–prop-2-ynyl product ratios varied dramatically with substituents on the tin, and identical products were obtained when the same 'ate' complex was formed from different precursors [Fig. 1(*c*)–(*f*), Table 1 entries 3–8]. However, the transient species undergoing silylation (species T) is probably not the 'ate' complex, since the Me_3SiCl *vs.* Pr^iMe_2SiCl selectivity for the *in situ* double trapping experiment using **1A** did not vary significantly when methyllithium or phenyllithium was used in the Li/Sn exchange. Nor would the ate complex be expected to have the low selectivity which was observed. Rather, the 'ate' complex must play a crucial role in determining the partitioning between species T and S.

Our best hypothesis is summarized in Scheme 1. ^{7}Li NMR studies of tin and other 'ate' complexes have shown that all are solvent-separated ion pairs (SSIP) in THF or THF–HMPA.[1b,c] We propose that the key intermediate 'ate' complexes **8A** or **8P** undergo three competitive process: (*i*) unimolecular (S_E1) fragmentation of the C–Sn bond to give a transient SSIP (species T), (*ii*) electrophilic attack by a lithium cation (S_E2) to give the stable contact ion pair (CIP, species S),[5] and (*iii*) equilibration between **8A** and **8P** by a [1,3] sigmatropic process.[6] The essence of our proposal is that the SSIP formed by the S_E1 process is so reactive[7] that silylation (k_2) is faster than ion pair recombination (k_1), and that some fraction of it can be trapped by silyl chloride before it decays to the CIP.[8] It is competition between the k_2 and k_1 processes which accounts for the steady increase in allenyl product as the concentration of Me_3SiCl is increased (Fig. 1).

All of the diverse features of the reaction are explained by this mechanism. The regiochemistry of the silylation is appropriate: the CIP reacts at the site remote from the C–Li, whereas the SSIP reacts at the site of highest charge density. Strongly coordinating solvents should selectively inhibit the S_E2 process (less electrophilic lithium), and increase the lifetime of the 'ate' complexes.[1b] Thus allenyl and prop-2-ynyl stannanes give identical results in THF–HMPA, and more of species T is trapped. For the least stable 'ate' complex intermediates in THF (**8A** and **8P**, R = Me) even the [1,3] sigmatropic equilibration no longer competes with the S_E1 process, and different allenyl to prop-2-ynyl product ratios are formed from **1A** and **1P** [Fig. 1(*a*), (*b*)].[9]

In summary, the Li/Sn exchange of **1A** and **1P** produces a transient reactive intermediate which can be trapped by some electrophiles. The tin 'ate' complexes formed during the Li/Sn exchange reaction play a crucial role in determining the partitioning of the reaction path between this intermediate (which may be a SSIP) and the stable organolithium reagent.

We thank the National Science Foundation and the Petroleum Research Fund, administered by the ACS, for support of this work.

Received, 28th April 1993; Com. 3/02448B

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