about 3×10^8 *slower* under the same conditions (k_1 for acid-catalyzed decomposition of $PhSSO_3^-$ in 60% dioxane containing 0.01 M $HClO_4$ at 25 °C is calculated[6] to be only $4 \times 10^{-9}\ s^{-1}$). The Bunte salt *S*-oxide is thus *over 10^8 less stable* in acid solution than a similar Bunte salt. One important contributor to this phenomenal difference in stability is almost certainly the much greater basicity of the sulfinyl function in the *S*-oxide as compared to the sulfide sulfur in the Bunte salt, i.e., K_{a2} in eq 2 $\ll K_a'$ in eq 3. Sulfinyl groups are known to be much more basic than analogously substituted sulfide groups.[7]

Given the interesting chemical behavior and high reactivity shown by **2**, we are now searching for a synthetic route that will permit the preparation of a simple Bunte salt *S*-oxide containing no other functional group than the $-S(O)SO_3^-$ function.

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(1) This research supported by the Robert A. Welch Foundation (Grant D-650).

(2) M. M. Chau and J. L. Kice, *J. Org. Chem.*, in press.

(3) Upon being heated in a melting point tube a sample of **2** begins to undergo slow thermal decomposition at slightly above 40 °C. This thermal decomposition of the solid, which is rapid at 70 °C, appears to lead to the formation of significant amounts of sulfur trioxide. The other products of the decomposition have not been identified, but do not melt below 300 °C.

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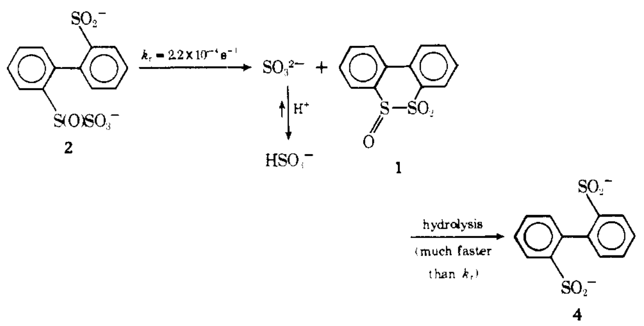
(5) Formation of disulfinate **4** from **2** in the acetate buffer occurs by rate-determining slow reversion of **2** to **1** plus sulfite, followed by rapid hydrolysis of **1** to **4**. In the acetate buffer sulfite is protonated to HSO_3^- as soon as it is formed, preventing the reverse reaction of **1** with sulfite.



(6) J. L. Kice, J. M. Anderson, and N. E. Pawloski, *J. Am. Chem. Soc.*, **88**, 5245 (1966).

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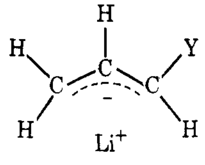
A General Route to Terminally Substituted Allylic Derivatives of Silicon and Tin. Preparation of Allylic Lithium Reagents

Summary: Wittig reactions of the appropriate β-trimethylstannyl- and β-trimethylsilylethyltriphenylphosphonium salt-derived ylides ($Ph_3P{=}CHCH_2SnMe_3$, $Ph_3P{=}CHCH_2SiMe_3$, $Ph_3P{=}C(Me)CH_2SiMe_3$ in the examples presented) with aldehydes and ketones provide a useful, general route to allylic compounds of silicon and tin.

Sir: We have reported recently concerning the synthesis and the unusual regioselectivity of *gem*-dichloroallyllithium in carbonyl addition reactions.[1] The results of this study prompted further interest in unsymmetrically substituted allyllithium reagents of general types **1** and **2**. Three major routes are available for the synthesis of allylic lithium reagents: direct lithiation of olefins,[2] allyl ether cleavage with metallic lithium,[3] and transmetalation reactions of allylic derivatives of heavy metals, principally of tin and lead.[1,4]



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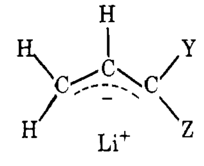


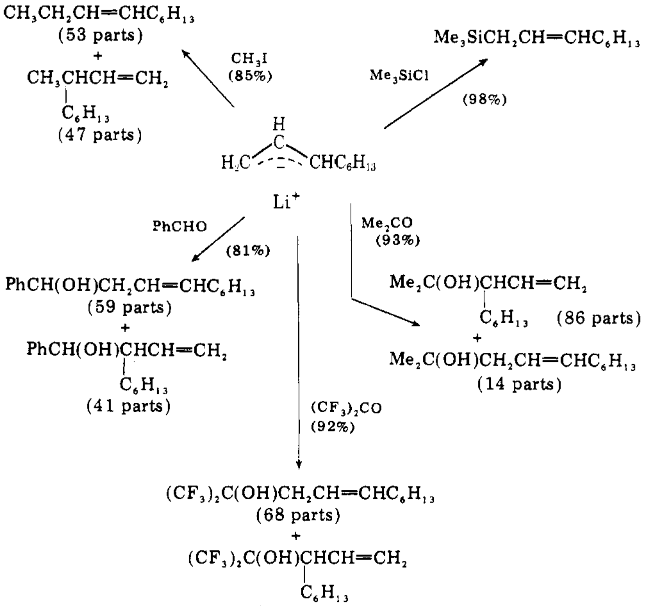
2

We describe here a new, general route to allylic derivatives of tin of types **3** and **4**. These are useful starting materials

$$\underset{\mathbf{3}}{Me_3SnCH_2CH{=}CHR} \qquad \underset{\mathbf{4}}{Me_3SnCH_2CH{=}CRR'}$$

for allylic lithium reagents of types **1** and **2**, where Y and Z = alkyl and aryl. Our new allyltin synthesis has added impor-

Scheme I. Reactions of *n*-Hexylallyllithium



Scheme II. Reactions of 1,1-Cyclopentamethyleneallyllithium

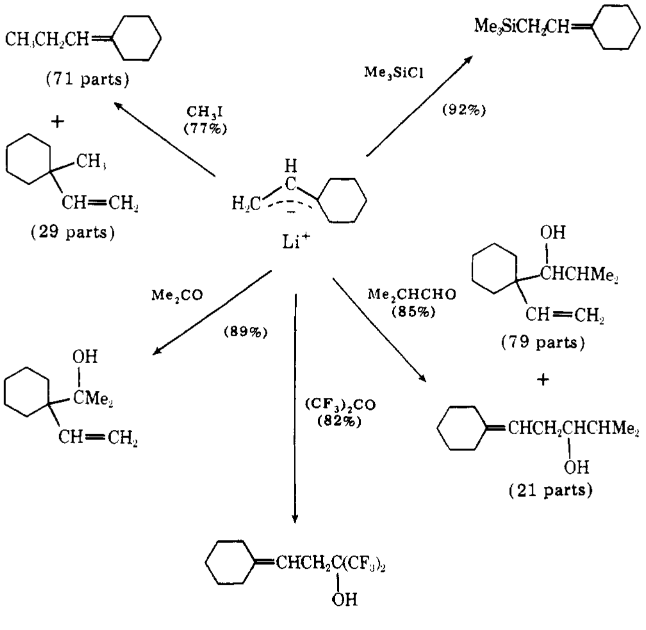
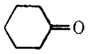
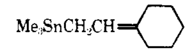
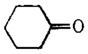
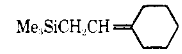
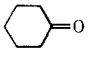
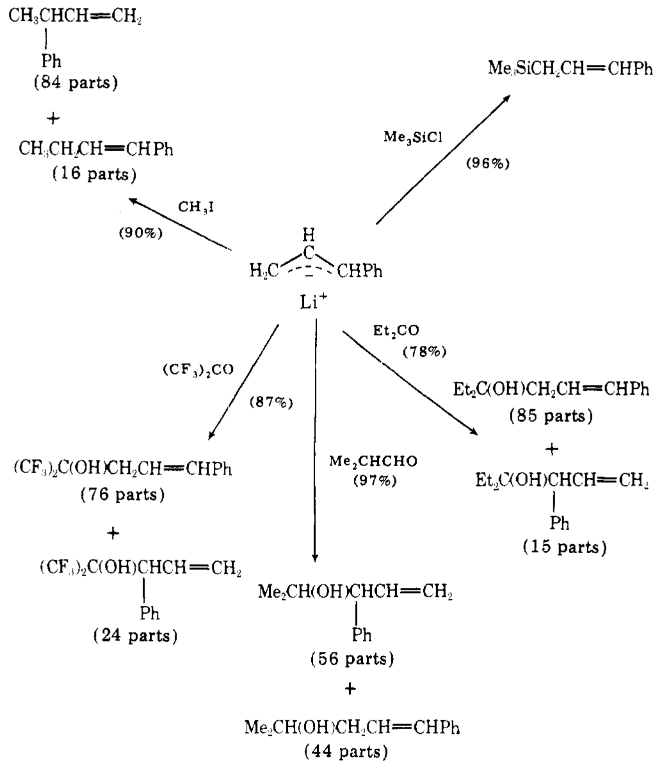


Table I. Preparation of Allylic Silicon and Tin Compounds[a]

Ylide reagent	Carbonyl reactant	Allylic product (% yield)	Trans/cis ratio
$Ph_3P{=}CHCH_2SnMe_3$	$n\text{-}C_6H_{13}CH{=}O$	$Me_3SnCH_2CH{=}CHC_6H_{13}\text{-}n$ (98)	70/30
		 (79)	
	$C_6H_5CH{=}O$	$Me_3SnCH_2CH{=}CHC_6H_5$ (70)	95/5
$Ph_3P{=}CHCH_2SiMe_3$	$n\text{-}C_6H_{13}CH{=}O$	$Me_3SiCH_2CH{=}CHC_6H_{13}\text{-}n$ (71)	75/25
		 (85)	
	$C_6H_5CH{=}O$	$Me_3SiCH_2CH{=}CHC_6H_5$ (63)	64/36
	$(C_2H_5)_2C{=}O$	$Me_3SiCH_2CH{=}C(C_2H_5)_2$ (38)[b]	
	$(CF_3)_2C{=}O$	$Me_3SiCH_2CH{=}C(CF_3)_2$ (43)	
$Ph_3P{=}C(CH_3)CH_2SiMe_3$	$C_2H_5CH{=}O$	$Me_3SiCH_2C(CH_3){=}CHC_2H_5$ (74)	55/45[c]
	$C_6H_5CH{=}O$	$Me_3SiCH_2C(CH_3){=}CHC_6H_5$ (72)	50/50
		(deprotonation regenerated the starting phosphonium salt)	

[a] Reactions were carried out in THF medium. The reactants were mixed at room temperature and the reaction mixture was stirred and heated at reflux under nitrogen for 12–15 h. Trap-to-trap distillation at 0.05–0.1 mm into a receiver cooled to −78 °C gave a solution of the product, which was analyzed by GLC. In larger preparative-scale reactions the product was isolated by vacuum distillation. [b] The procedure in a gave only a yield of 27%. In this reaction the THF solvent was replaced by toluene and the reaction mixture then was heated at reflux for 40 h. [c] Stereochemistry was not assigned.

Scheme III. Reactions of Phenylallyllithium



tance in view of the newly developed utility of the allyltin compounds themselves in organic and organometallic synthesis.[5] Furthermore, this general procedure can be extended to the synthesis of allylsilicon compounds analogous to **3** and **4**, and, although this has not yet been examined, also of allyl compounds of germanium and lead. This is of interest, since allylsilanes also have found useful applications in organic synthesis in recent years.[6]

The general concept involved in our allylmetallics synthesis is based on an allyltin preparation of Hannon and Traylor.[7] These workers used the reaction of trimethyltinlithium with vinyltriphenylphosphonium bromide to prepare the ylide $Ph_3P{=}CHCH_2SnMe_3$, which could be used in a Wittig reaction with cyclohexanone.[8] In our hands, however, this procedure gave only moderate yields of the expected allyltin compound, $Me_3SnCH_2CH{=}C_6H_{10}\text{-}c$ (44%, Wittig reaction at −93 °C; 48%, at room temperature), based on the 1:1 Me_3SnLi/$[Ph_3PCH{=}CH_2]Br$ stoichiometry used, and, moreover, a considerable portion (~50%) of the trimethyltinlithium was converted to hexamethylditin during the course of the reaction.

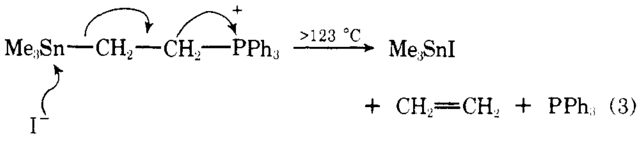
Our new procedure uses the same Wittig reagent, but involves a different preparation, as shown in eq 1 and 2.

$$Ph_3P{=}CH_2 + Me_3MCH_2I \rightarrow [Ph_3PCH_2CH_2MMe_3]I \quad (1)$$
$$(M = Sn, Si)$$

$$[Ph_3PCH_2CH_2MMe_3]I + RLi \rightarrow Ph_3P{=}CHCH_2MMe_3 + RH + LiI \quad (2)$$
$$(R = (Me_2CH)_2N \text{ when } M = Sn;\ R = CH_3 \text{ when } M = Si)$$

The phosphonium halides, $[Ph_3PCH_2CH_2SnMe_3]I$ and $[Ph_3PCH_2CH_2SiMe_3]I$, were isolated in better than 85% yield and were fully characterized. That this procedure is extendable to the synthesis of $[Ph_3PCH(R)CH_2MMe_3]I$ salts was demonstrated by the preparation of $[Ph_3PCH(Me)CH_2SiMe_3]I$ by reaction of $Ph_3P{=}CHCH_3$ with Me_3SiCH_2I. This procedure is simple and easily carried out. The preparation of the required phosphorus ylides presents no special difficulties, and the iodomethyl compounds are fairly easily prepared; Me_3SiCH_2I by the action of sodium iodide in anhydrous medium on the readily available Me_3SiCH_2Cl,[9] and Me_3SnCH_2I by the reaction of ICH_2ZnI with trimethyltin chloride.[10] The ethereal phosphorus ylide solution is added slowly to the cooled (ice bath) ether solution of the iodomethyl compound (nitrogen atmosphere). The reaction mixture is stirred at room temperature for 12–15 h and then the phosphonium halide which was precipitated is filtered. In the case of the $Ph_3P{=}CH_2/Me_3SnCH_2I$ reaction, the phosphonium salt product was obtained admixed with 10–15% of $[Ph_3PMe]I$. Although this impurity may be removed by fractional crystallization, such processing is rather wasteful. Since the impurity in subsequent Wittig reactions gives olefinic products which are much more volatile (and hence easily separated) than the allyltin products, it is our usual practice to use the crude $[Ph_3PCH_2CH_2SnMe_3]I$ after its purity has been assessed by NMR spectroscopy.

The β-trimethylstannylethylphosphonium iodide undergoes thermal decomposition at its melting point, evolving ethylene in a β-elimination reaction (eq 3), but the silicon



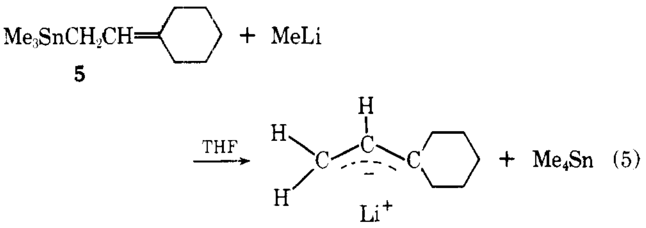
$$I^- \; Me_3Sn{-}CH_2{-}CH_2{-}\overset{+}{P}Ph_3 \xrightarrow{>123\ ^\circ C} Me_3SnI + CH_2{=}CH_2 + PPh_3 \quad (3)$$

analogue is stable well above its melting point of 163–164.5 °C.

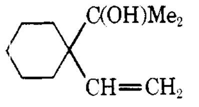
The β-stannyl- and β-silyl-substituted phosphonium halides may be deprotonated to the respective ylides, both of which form deep red-orange solutions in diethyl ether and in tetrahydrofuran. Methyllithium serves well as the base in the case of $[\mathrm{Ph_3PCH_2CH_2SiMe_3}]\mathrm{I}$ and $[\mathrm{Ph_3PCH(CH_3)CH_2SiMe_3}]\mathrm{I}$, but for the deprotonation of $[\mathrm{Ph_3PCH_2CH_2SnMe_3}]\mathrm{I}$, lithium amides, $\mathrm{R_2NLi}$ (R = $\mathrm{Me_2CH}$ or $\mathrm{Me_3Si}$), must be used, since organolithium reagents do not react regiospecifically, attacking in part at tin as well as at the protons α to phosphorus. The ylides formed, $\mathrm{Ph_3P{=}CHCH_2SnMe_3}$, $\mathrm{Ph_3P{=}CHCH_2SiMe_3}$, and $\mathrm{Ph_3P{=}C(Me)CH_2SiMe_3}$, react readily with aldehydes and, in general, somewhat less well with ketones, to give the expected allylstannanes and allylsilanes (eq 4; Table I).

$$\mathrm{Ph_3P{=}CHCH_2MMe_3 + RR'C{=}O \xrightarrow{THF} Me_3MCH_2CH{=}CRR' + Ph_3PO} \quad (4)$$

The three allylic tin compounds in Table I undergo ready conversion to the respective allylic lithium reagents, e.g., eq 5. In a typical reaction, **5** (3.74 mmol) in 200 mL of dry THF at 0 °C, under nitrogen, was treated with 4.1 mmol of methyllithium in diethyl ether. The resulting yellow solution was stirred for 30 min at 0 °C and then 20 mmol of acetone was added. After the reaction mixture had been stirred at room temperature for 30 min, hydrolytic workup was followed by GLC analysis of the organic phase to establish the presence of **6** in 89% yield. The results of these experiments are illustrated in Schemes I–III. The product yields are uniformly excellent. A discussion of the observed regioselectivities in the reactions of these ambident reagents will be deferred until this study has been completed.



(5)



6

It is obvious that this new route to allylic compounds of silicon and tin should be quite general in its scope of applicability. By appropriate variation of the phosphorus ylide and the carbonyl substrate in these reactions, allylic derivatives of silicon and tin of type $\mathrm{Me_3MCH_2C(R){=}CR'R''}$, where R, R′, and R″ should be capable of wide variation, should be accessible. The allyltins thus prepared would provide starting materials for many new allylic lithium reagents. In many cases the direct lithiation procedure, the reaction of RLi/Lewis base or $\mathrm{RLi/Me_3COK}$ with an appropriate unsaturated hydrocarbon, would provide the simplest route to the desired allylic lithium reagent.[2] However, the additives which usually are required to effect such metalations may not always be compatible with other functionality in the carbonyl reactant or may interfere in other ways. Also, there will be instances when the appropriate unsaturated hydrocarbon is not available. Thus the versatility of our new procedure and its ease of application may prove very useful in organic and organometallic synthesis.

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(8) Cyclohexanone (in unspecified amount) was added to the red ylide solution to the point of color discharge. A 90% yield of $\mathrm{c\text{-}C_6H_{10}{=}CHCH_2SnMe_3}$ product, *based on cyclohexanone*, was reported.[7] This information, of course, gives no indication of the efficiency of the total process, so that its true synthetic utility cannot be evaluated.

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Conjugate Addition–Elimination in the Reaction of *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes with 4-Methoxy-3-buten-2-one and Related Derivatives. A Convenient New Route to Conjugated Enynones

Summary: *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes (*B*-1-alkynyl-9-BBN), easily and quantitatively prepared by the reaction of boron trifluoride diethyl etherate with the corresponding lithium methyl alkynyldialkylborinate,[1] undergo a remarkably facile reaction with the readily available 4-methoxy-3-buten-2-one and related derivatives in hexane at room temperature to provide, in excellent yield, conjugated enynones.

Sir: Recently we described the conjugate addition of *B*-1-alkynyl-9-borabicyclo[3.3.1]nonanes to a variety of α,β-unsaturated ketones, which provided a valuable synthesis of γ,δ-alkynyl ketones.[2] House has suggested that reduction potentials may be used to determine the suitability of substrates toward conjugate addition of organocuprates and perhaps other organometallic reagents.[3] Hooz and Layton, in their work on dialkylalkenyl alanes and dialkylalkynyl alanes, point out that the yields of conjugate addition product appear to correlate well with the reduction potentials of the substrates utilized.[4]