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Preparation and Reactions of Water Stable Hypervalent 10-Sn-5 Allyl Ate Complexes

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ABSTRACT: *Hypervalent 10-Sn-5 allyl and crotyl tin ate complexes bearing Martin ligands were prepared and found to be surprisingly stable in water. These compounds were found to react with aldehydes in the presence of weak Lewis acids such as LiBr to give the corresponding homoallyl alcohols. Product analysis of the reaction of the crotyl compounds indicated that the reaction occurred via a cyclic transition state unlike an acyclic transition state operative for widely utilized allyltrialkyltin reagents that are of ordinary valency.* Heteroatom Chem 12:425–431, 2001

INTRODUCTION

The allylation reaction has enjoyed widespread application in organic synthesis as a means of introducing new C–C bonds, especially because the allyl group can undergo further manipulation to provide other functional groups [1]. The unique mode of reaction (type II, acyclic transition state) differing from that of other allylborane or allylmetal reagents (type I, cyclic transition state) has made allyl and crotylstannanes attractive complementary reagents [2]. Chiral allylic reagents have led to the stereocontrolled synthesis of chiral polypropionates and carbohydrates [3], and the development of catalytic asymmetric reactions has widened the synthetic scope of tin reagents [4]. Among allylmetal compounds, it has been found that hypervalent allylsilicate compounds bearing oxygens or fluorines as the remaining coordinating atoms also undergo the allylation reaction and in a manner (type I) differing from that of the corresponding normal valent allylsilanes (type II) [5,6]. The utility of hypervalent allylsilane compounds has been enhanced by the discovery that allylsilyltrichloride reacts under mild conditions in the presence of donor solvents [7]. Although examples are still limited, hypervalent tin is also gradually finding a place as a group of reagents useful for organic synthesis. Notable examples are as an anhydrous source of fluoride [8], and as aryl and alkyl donors in cross coupling reactions [9]. As for allylation reactions, there is little precedence, and the only examples we are aware of are the uses of ate complexes, bearing tartaric ester ligands generated in situ, in asymmetric allylation reactions [10,11]. We have had a long interest in hypervalent compounds, and during the course of the examination of the reactivity of water stable hypervalent 10-Sn-5 compounds [12], we have found that hypervalent 10-Sn-5 allyltin compounds bearing Martin's ligands as bidentates undergo allylation, while corresponding allylsilane reagents have been reported to be inactive [5]. Herein we report the details.

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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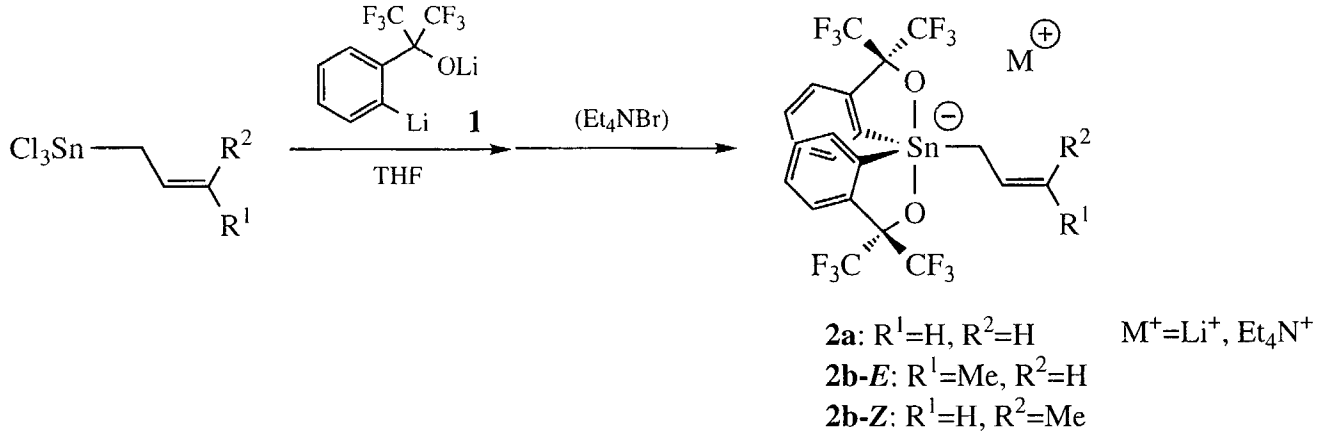
RESULTS AND DISCUSSION

Preparation of allyl tin ate complex **2** was carried out according to Scheme 1. Two equivalents of lithium 1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide **1** (prepared by the method described by Martin et al. [13]) was added to allyltin(IV) chloride (prepared according to a reported disproportionation method [14]) in tetrahydrofuran (THF) at −78°C, followed by treatment with Et_4NBr to give the allyl compound **2a-Et$_4$N$^+$** in 60% yield. Counterion exchange was required since the allylic compound with lithium as the countercation was found to be rather unstable to aqueous workup, whereas that with the ammonium countercation was found to be perfectly stable at ambient temperatures. Since the same method could not be used for the synthesis of crotyl compounds, due to the expected facile isomerization of the crotyl moiety [2], we used a modified method that does not require heating for the preparation of allyltin(IV) trihalide, from allyl halide and tin(II) halide, to minimize isomerization [15]. Immediately after mixing crotyl chloride (ca. 9:1 mixture of *E-Z* isomers) and tin dichloride in THF at 0°C, the solution was added to a THF solution of two equiv. of **1** at −78°C, affording the crotyl compound (a mixture of *E-Z* isomers in 80:20 ratio) in 51% yield after counterion exchange with Et_4NBr. The ^{119}Sn NMR chemical shift of the allyl compound **2a-Et$_4$N$^+$** was δ −105.0 (CD_3CN), while that of the crotyl mixture **2b-Et$_4$N$^+$** was δ −104.9, −105.3 (acetone-d_6). These high-field chemical shifts are a clear indication that the compounds are pentacoordinate [16]. In ^{1}H NMR spectra, the protons of the aryl groups ortho to tin showed characteristic downfield shifts also seen for neutral pentacoordinate compounds [17], and the spectra as a whole was indicative of a C_2 symmetric structure in which the oxygen atoms of the bidentate are located in apical positions, as expected for pentacoordinate compounds of ordinary structure. The ^{19}F NMR spectra showed only a pair of quartets, implying the presence of only two different fluorine groups and they did not coalesce in the temperature range of −60°C to 100°C. This indicated that the pseudorotation of the tin compounds was unobservable on the NMR timescale, thereby giving a lower limit for the barrier as at least $\Delta G^{+} = 21$ kcal mol^{-1} [18].

Initial investigations were carried out with the allyl ate complex **2a-Li$^+$** generated in situ without countercation exchange as tabulated in Table 1. The ate complex was found to react with aromatic aldehydes (Table 1, entries 1 and 2) smoothly at room temperature (rt) giving homoallylic alcohols along with an insoluble substance likely to be hydroxylated tin ate complex **3** or oligomeric material originating from **3**. The α-branched alkyl aldehyde, 2-phenylpropionaldehyde, was also found to react (entry 3); however, the α-unbranched alkyl aldehyde, 3-phenylpropionaldehyde, gave hardly any expected product, even after prolonged reaction periods (entry 4). We reasoned that this was due to undesired side reactions induced by basic contaminants present because of incomplete transformation to the ate complex. In order to minimize the affect of these species, the ate complex solution was filtered through a bed of Celite prior to use. The ate complex solution treated in this way gave rise to the desired product in an improved yield of 46% (entry 5). The reaction of a ketone (acetophenone) proved to be sluggish (entry 6), probably due to steric hindrance. The reaction of 2-phenylpropionaldehyde gave rise to a mixture of diastereomers in a ratio of 4:1 in favor of the *syn* product. This complies with predictions from the Felkin-Anh model, and, interestingly, the ratio is



SCHEME 1

TABLE 1 The Reactions of Allyl Ate Complex **2a-Li**$^+$ Prepared In Situ

Entry	*Carbonyl Compound*	*Conditions*[a]	*Yield (%)*
1	PhCHO	rt, 19 hours	78
2	4-$MeOC_6H_4CHO$	rt, 20 hours	66
3	$PhCH(CH_3)CHO$	rt, 16 hours	72 (4:1)[c]
4	$PhCH_2CH_2CHO$	rt, 8.5 days	6
5	$PhCH_2CH_2CHO$	rt, 19 hours[b]	46
6	$PhCOCH_3$	reflux, 67 hours	5

[a]Carried out in THF.
[b]The ate complex solution was passed through a bed of Celite prior to use.
[c]The syn:anti ratio is in parenthesis.

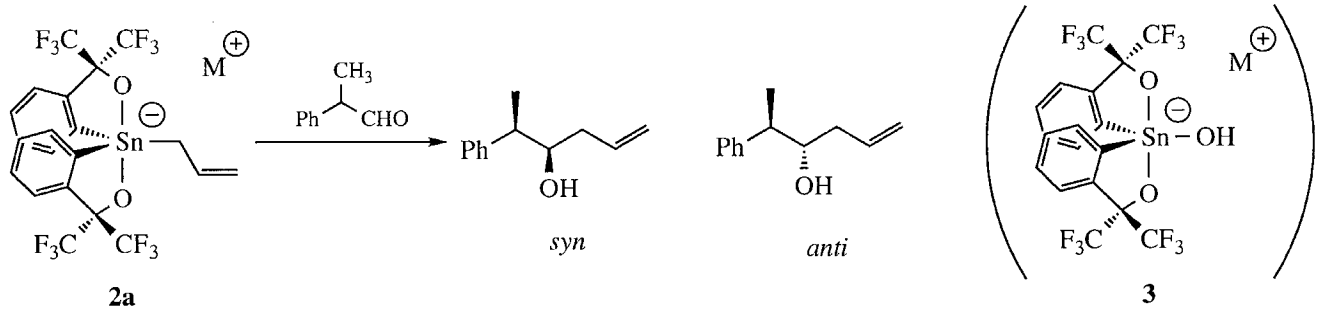
about the same as in the reaction of allyltributyltin with the aldehyde promoted by Lewis acids at lower temperatures [2a,b,19].

To eliminate the need to prepare the fresh reagent for every reaction, we decided to examine the storability of the ammonium salt **2a-Et$_4$N**$^+$. The results are given in Table 2. Contrary to expectation, the ate complex was found to be inert and did not react with 2-phenylpropionaldehyde even at reflux temperature (Table 2, entry 1). This implied that some ingredients in the solution of the in situ freshly prepared ate complex **2a-Li**$^+$ had activated the reaction. To elucidate the components, several additives were examined with 2-phenylpropionaldehyde as substrate. Since Li^+ seemed to be the best candidate, several lithium salts were examined. Although reflux temperature was required, the reaction did proceed, regardless of the counteranion (Cl^-, Br^-, F^-, BF_4^-; entries 2–7). Since the result upon using $LiBF_4$ was comparable with the others, the main source of activation could be concluded to be Li^+. An examination of the effects of two ammonium halides resulted in obvious acceleration, but to a lesser extent than with Li^+ salts present, as indicated by the required reaction times and lower yields (entries 8 and 9). A Lewis acid frequently used in allyltin chemistry of ordinary valency, $BF_3 \cdot OEt_2$, was found to accelerate the reaction, but led to a somewhat lower yield (entry 10). Since the reactivity attained for **2a-Li**$^+$, prepared in situ, could not be reproduced when the other additives were present, unreacted or only partially transformed allyltin chloride became the suspected cocatalyst. Addition of a catalytic amount of allyltin chloride reproduced the results obtained from the in situ reaction (entry 11). The effectiveness of Li^+ as a promoter in the reaction of the allyl ate complex was thus unveiled. The diastereoselectivity ratio was found to be comparable with that of **2a-Li**$^+$ in some cases, although the reaction was carried out at a higher temperature. The reaction of benzaldehyde was also found to be activated by Li^+ (entries 12, 13).

Allylation reactions of allyltin reagents generally take place via one of two transition states. Water stable tetraorganotin reagents of ordinary valency are believed to react via acyclic transition states (type II), while tetravalent reagents with halogen substituents [2d] and a hypervalent reagent [11], which are all susceptible to water, have been suggested to proceed via cyclic transition states (type I). Discrepancy between the two paths is usually examined by the reaction of crotyl reagents, in which the former group of reagents favor the *syn* product regardless of the geometry of the reagent, whereas reagents of the latter group undergo stereospecific reactions, that is, the *E*-crotyl reagent leads to the *anti* product, while the Z-crotyl reagent gives the *syn* product. Thus, the reactions of the *E*-rich crotyl reagent were examined more thoroughly.

In order to see whether the reagent was prone to geometric isomerization, reagent mixtures of two different ratios (*E:Z* = 80:20 and 64:36) were subjected to the standard reaction conditions of allylation (LiBr, reflux). Neither mixture underwent more than 3% change in ratio over a period of 4 days, thus establishing the reliability of the forthcoming reaction stereochemical results.

As the substrate, 4-nitrobenzaldehyde was utilized to facilitate the reaction. Scheme 3 and Table 3 summarize the results. Reexamination of the reaction under nonadditive conditions for this substrate revealed that the reaction is actually accelerated as expected to give the anticipated product in moderate yield (Table 3, entry 1). However, the diastereomeric ratio was low. The reaction in the presence of LiBr was found to proceed even at rt, giving the *anti* product in preference (entry 2). Indications were that the reaction proceeded via a cyclic transition state. This stereoselectivity also provided evidence that the ate complex is the reacting species and not dissociated crotyl lithium, which is reckoned to give unselective product mixtures [1]. The use of less reactive aromatic aldehydes revealed that, although higher temperatures were required, stereoselectivity was retained to a high degree (entries 3–5) [20]. The use of LiF, which is a fluorine source, and $LiBF_4$, which is a potential fluorine source, led to some decrease in the diastereomeric ratio (entries 6 and 7). Unexpectedly, $LiClO_4$ also led to a decrease (entry 8). The validity of $MgBr_2$ was also revealed (entry 9). The use of solvents with donor ability higher than THF led to lower reactivity, and the diastereomeric ratio decreased, especially in the case of dimethylformamide (DMF) (entries 10 and 11). The use of Lewis acids usually employed in reactions of ordinary valent



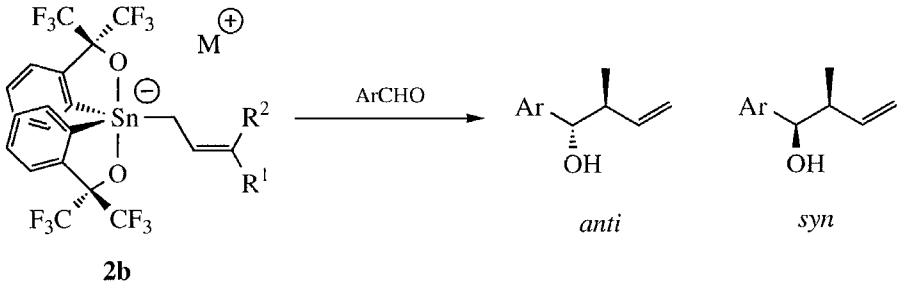
2a **3**

SCHEME 2

TABLE 2 The Reactions of Isolated Allyl Ate Complex **2a-Et$_4$N$^+$**

Entry	*Aldehyde*	*Solvent*	*Additive*	*Conditions*	*Yield (%)*[a]
1	$PhCH(CH_3)CHO$	THF	none	reflux	0
2	$PhCH(CH_3)CHO$	THF	LiCl (4 equiv.)	reflux, 45 hours	80 (4:1)
3	$PhCH(CH_3)CHO$	THF	LiCl (1 equiv.)	reflux, 45 hours	57 (3.7:1)
4	$PhCH(CH_3)CHO$	CH_2Cl_2 + THF	LiCl (1 equiv.)	reflux, 89 hours	49 (5:1)
5	$PhCH(CH_3)CHO$	THF	LiBr (4 equiv.)	reflux, 32 hours	80 (nd)[b]
6	$PhCH(CH_3)CHO$	THF	LiF (4 equiv.)	reflux, 45 hours	62 (nd)[b]
7	$PhCH(CH_3)CHO$	THF	$LiBF_4$ (4 equiv.)	reflux, 45 hours	74 (2.4:1)
8	$PhCH(CH_3)CHO$	CH_2Cl_2	Et_4NCl (1 equiv.)	reflux, 145 hours	44 (1.6:1)
9	$PhCH(CH_3)CHO$	CH_2Cl_2 + THF	Bu_4NF (1 equiv.)	reflux, 114 hours	10 (2:1)
10	$PhCH(CH_3)CHO$	CH_2Cl_2	$BF_3 \cdot OEt_2$	rt, 44 hours	32 (2.4:1)
11	$PhCH(CH_3)CHO$	$CHCl_3$	$AllylSnCl_3$ (0.1 equiv.) + LiBr (4 equiv.)	rt, 6 hours	65 (nd)[b]
12	PhCHO	THF	none	reflux	0
13	PhCHO	$CHCl_3$ + THF	LiBr (4 equiv.)	rt, 15 hours	88

[a]The *syn:anti* ratio is in parenthesis.
[b]Not determined.



2b

SCHEME 3

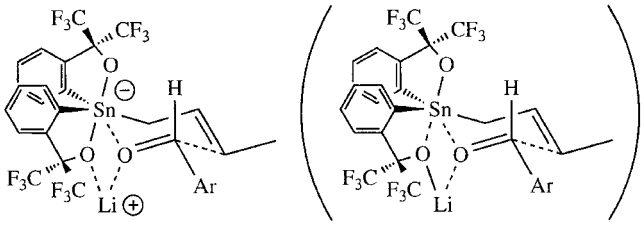
allyltin reagents was also examined. The reaction using $BF_3 \cdot OEt_2$ proceeded at 0°C and resulted in a reversal in selectivity in favor of the syn product (entry 12). In order to determine whether the product ratio was dependent on the *E:Z* ratio of the ate complex, a reagent with 64:36 composition was also examined, and the results turned out the same (entry 13). This is an indication that, in the case of $BF_3 \cdot OEt_2$, the major pathway is via the acyclic path. The use of other Lewis acids resulted in nearly 1:1 mixtures (entries 14–16). In these instances, the involvement of other active allyl species are implemented by the low selectivity, as in the case of **2a-Li$^+$**.

The plausible transition state is depicted in Scheme 4. Since a cyclic transition state is implemented by the selectivity in the reaction of the crotyl reagents, the carbonyl oxygen apparently interacts with the Lewis acidic tin atom to form the chair form ring. The role of Li^+ as activator can be rationalized to be a chelating agent between the carbonyl oxygen and one of the ligand oxygens, and, in turn, as an activator of the Lewis acidic tin atom by withdraw-

TABLE 3 The Reactions of Isolated Crotyl Ate Complex **2b-Et$_4$N$^+$**[a]

Entry	*Aldehyde*	*Solvent*	*Additive*	*Conditions*	*Yield (%)*[b]
1	4-$O_2NC_6H_4CHO$	$CHCl_3$ + THF	none	reflux, 168 hours	53 (55/45)
2	4-$O_2NC_6H_4CHO$	$CHCl_3$ + THF	LiBr (4 equiv.)	rt, 14 hours	88 (75/25)
3	4-ClC_6H_4CHO	$CHCl_3$ + THF	LiBr (4 equiv.)	reflux, 19 hours	85 (78/22)
4	PhCHO	$CHCl_3$ + THF	LiBr (4 equiv.)	reflux, 18 hours	96 (78/22)
5	4-$MeOC_6H_4CHO$	$CHCl_3$ + THF	LiBr (4 equiv.)	reflux, 17 hours	64 (76/24)
6	4-$O_2NC_6H_4CHO$	$CHCl_3$ + THF	LiF (4 equiv.)	40°C, 4 hours	71 (61/39)
7	4-$O_2NC_6H_4CHO$	$CHCl_3$ + THF	$LiBF_4$ (4 equiv.)	rt, 14 hours	85 (55/45)
8	4-$O_2NC_6H_4CHO$	$CHCl_3$ + THF	$LiClO_4$ (4 equiv.)	reflux, 4 hours	91 (70/30)
9	4-$O_2NC_6H_4CHO$	$CHCl_3$ + THF	$MgBr_2$ (4 equiv.)	rt, 23 hours	93 (76/24)
10	4-$O_2NC_6H_4CHO$	CH_3CN	LiBr (4 equiv.)	reflux, 22 hours	91 (74/26)
11[c]	4-$O_2NC_6H_4CHO$	DMF	LiBr (4 equiv.)	50°C, 45 hours	81 (56/44)
12	4-$O_2NC_6H_4CHO$	CH_2Cl_2	$BF_3 \cdot OEt_2$ (1 equiv.)	0°C, 12 hours	93 (31/69)
13[d]	4-$O_2NC_6H_4CHO$	CH_2Cl_2	$BF_3 \cdot OEt_2$ (1 equiv.)	0°C, 12 hours	88 (32/68)
14	4-$O_2NC_6H_4CHO$	CH_2Cl_2	Me_3SiOTf (1 equiv.)	0°C, 24 hours	80 (45/55)
15	4-$O_2NC_6H_4CHO$	CH_2Cl_2	$SnCl_4$ (0.1 equiv.)	0°C, 12 hours	93 (47/53)
16	4-$O_2NC_6H_4CHO$	CH_2Cl_2	$TiCl_4$ (0.1 equiv.)	0°C, 12 hours	89 (46/54)

[a]The *E/Z* ratio of the crotyl reagent **2b-Et$_4$N$^+$** was 80:20, unless otherwise noted.
[b]The *anti:syn* ratio is in parenthesis.
[c]The *E/Z* ratio of the crotyl reagent was 75:25.
[d]The *E/Z* ratio of the crotyl reagent was 64:36.



SCHEME 4 Plausible Transition State for the Reaction of (*E*)-Crotyl Ate Complex **2b-Et$_4$N$^+$** Leading to the *anti* Product

ing electron density from the atom. Thus, there is probably some contribution in the transition state from the limiting structure shown on the right. The interaction of Li^+ with one of the oxygen atoms of the ligand bonded to the tin is also suggested by ^{119}Sn NMR spectroscopy. The chemical shifts of **2b-Et$_4$N$^+$** were found to shift downfield to −103.5 from −104.9 and −105.3 upon addition of 10 equiv. of either $LiClO_4$ or LiBr, whereas no shift was observed for LiF, Bu_4NF, or Et_4NBr.

In summary, we have isolated the first water stable ammonium salts of allyltin ate complexes. The allylation reaction of the ate complexes readily gave allyl alcohols upon reaction with aldehydes provided that the lithium cation was present, via what we believe to be a cyclic transition state involving activation by the lithium cation.

EXPERIMENTAL

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz), ^{19}F (376 MHz), and ^{119}Sn (162 MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^{1}H NMR (90 MHz) and ^{19}F NMR (85 MHz) spectra were also routinely recorded on a Hitachi R-90H spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from internal Me_4Si, or from residual chloroform (δ = 7.26), acetonitrile (δ = 2.1), or acetone (δ = 2.0). ^{19}F NMR chemical shifts (δ) are given in ppm downfield from external $CFCl_3$. ^{119}Sn NMR chemical shifts (δ) are given in ppm downfield from external Me_4Sn. Elemental analyses were performed on a Perkin Elmer 2400CHN elemental analyzer.

All reactions were carried out under N_2. Tetrahydrofuran was freshly distilled from Na-benzophenone. CH_2Cl_2 and $CHCl_3$ were freshly distilled from CaH_2 prior to use. All other solvents and liquid reagents were distilled from CaH_2 and stored under inert atmospheres. Inorganic salts were all of anhydrous grade and were used as received. Preparative thin-layer chromatography was carried out on plates of Merck silica gel 60 GF254.

*Tetraethylammonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C^2,O] allylstannate (***2a-Et$_4$N$^+$***)*

To n-BuLi (1.59 M in hexane, 9.40 mL, 14.9 mmol), was added *N,N,N′,N′*-tetramethylethylenediamine (0.23 mL, 1.52 mmol), and the resulting solution was stirred for 20 minutes to allow the formation of a suspension. Then, THF (1 mL) was added to dissolve the precipitate, and 1,1,1,3,3,3-hexafluoro-2-phenyl-

2-propanol (1.20 mL, 7.18 mmol) was added dropwise at 0°C. After the solution had been stirred overnight at room temperature, THF (9 mL) was added to dissolve the newly formed precipitate, followed by the dropwise addition of allyltin(IV) chloride (0.50 mL, 3.56 mmol) at −78°C. The solution was allowed to warm to rt, and stirring was continued for a few hours. The solvent was removed in vacuo, and then dry CH_2Cl_2 (10 mL) was added to give a suspension. This was transferred to Et_4NBr (0.76 g, 3.60 mmol) in dry CH_2Cl_2 (10 mL), and the resulting mixture was stirred overnight. After careful filtration through Celite, the filtrate was concentrated, and the residue was recrystallized (CH_2Cl_2-benzene) to give colorless crystals containing one equivalent of benzene (1.83 g, 60%). A subsequent trial revealed that the product was not amenable to aqueous workup. Benzene could be removed by heating under reduced pressure. **2a-Et$_4$N$^+$** m.p. 147–148°C (dec); ^{1}H NMR (CD_3CN) δ 8.05–8.00 (m, 2 H), 7.7–7.6 (m, 2 H), 7.4–7.2 (m, 4 H), 6.30–5.78 (m, 1 H), 4.90–4.45 (m, 2 H), 3.12 (q, J = 7.3 Hz, 8 H), 1.99 (d, J = 8.1 Hz, 2 H), 1.18 (t of t, J = 7.3 Hz, $^3J_{^{14}N\text{-}H}$ = 1.9 Hz, 12 H). ^{19}F NMR (CD_3CN) δ −74.6 (q, J = 8.3 Hz, 6 F), −74.7 (q, J = 8.3 Hz, 6 F). ^{119}Sn NMR (CD_3CN) δ −105.0. Calcd for $C_{29}H_{33}F_{12}NO_2Sn$: C, 44.99; H, 4.30; N, 1.81. Found C, 44.90; H, 4.05; N, 2.11.

*Tetraethylammonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C^2,O] crotylstannate (***2b-Et$_4$N$^+$***)*

To n-BuLi (1.68 M in hexane, 25.5 mL, 43.3 mmol) was added *N,N,N′,N′*-tetramethylethylenediamine (0.62 mL, 4.1 mmol), and the resulting solution was stirred for 20 minutes to allow the formation of a suspension. Then, THF (10 mL) was added to dissolve the precipitate, and 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (3.17 mL, 20.6 mmol) was added dropwise at 0°C. After stirring of the solution overnight at room temperature, THF (25 mL) was added to dissolve the newly formed precipitate. To this mixture was added at −78°C a THF solution of crotyltin(IV) trichloride (16.9 mL, ca. 10.3 mmol content), prepared from tin(II) chloride (2.47 g, 13.0 mmol) and crotyl chloride (1.27 mL, 13.0 mmol) in THF (20 mL) at 0°C. The resulting solution was allowed to warm to rt and was stirred overnight. Countercation exchange, aqueous workup, and recrystallization (CH_2Cl_2-benzene) gave colorless crystals containing benzene (4.52 g, 51%, *E:Z* = 80:20). The amount of benzene varied and excessive heating in attempts to completely remove it led to partial decomposition. ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 6.8 Hz, $^3J_{^{119}Sn\text{-}H}$ = 26.5 Hz, 2 H), 7.64 (m, 2 H), 7.39–7.24 (m, 4 H), 5.70–5.61 (m, 1 H), 4.90–4.45 (m, 2 H), 2.54–2.50 (q, J = 7.3 Hz, 8 H), 1.99 (d, J = 8.1 Hz, 2 H), 1.18 (t of t, J = 7.3 Hz, $^3J_{^{14}N\text{-}H}$ = 1.9 Hz, 12 H). ^{119}Sn NMR (acetone-d_6) δ −104.9, −105.3. Calcd for $C_{30}H_{35}F_{12}NO_2Sn \cdot 0.5xC_6H_6$: C, 47.91; H, 4.63; N, 1.69. Found C, 47.70; H, 4.52; N, 1.46.

General Procedure for the Allylation Reactions

To a solution of an allyltin reagent (0.54 mmol) and LiBr (2.3 mmol) in a mixture of THF (9.3 mL) and CH_2Cl_2 (9.3 mL) was added an aldehyde (0.54 mmol) at rt. After having been stirred for the specified amount of time at the specified temperature, the solution was treated with aq NH_4Cl. Extraction with CH_2Cl_2 and treatment of the combined extracts with anhydrous $MgSO_4$, followed by removal of organic solvents, gave an oily substance. This was redissolved in hexane, and insoluble tin residues were removed by filtration. The crude mixture was then subjected to chromatographic treatment (SiO_2, CH_2Cl_2) to furnish the pure product.

1-Phenyl-3-buten-1-ol. ^{1}H NMR ($CDCl_3$) δ 7.43–7.23 (m, 5H), 6.04–5.58 (m, 1H), 5.28–5.03 (m, 2H), 4.70 (t, J = 7 Hz, 1H), 2.49 (t, J = 7 Hz, 2H), 2.10 (s, 1H).

1-(4-Methoxyphenyl)-3-buten-1-ol. ^{1}H NMR ($CDCl_3$) δ 7.25 (d, J = 9 Hz, 2H), 6.88 (d, J = 9 Hz, 2H), 6.03–5.57 (m, 1H), 5.22–5.02 (m, 2H), 4.66 (t, J = 7 Hz, 1H), 3.78 (s, 3H), 2.48 (t, J = 7 Hz, 2H), 2.08 (br s, 1H).

2-Phenyl-5-hexen-3-ol [2b,19]. ^{1}H NMR ($CDCl_3$) δ syn: 7.40–7.08 (m, 5H), 6.04–5.47 (m, 1H), 5.23–4.95 (m, 2H), 3.82–3.55 (m, 1H), 2.77 (quint, J = 7 Hz, 1H), 2.40–1.86 (m, 2H), 1.60 (br s, 1H), 1.35 (d, J = 7 Hz, 3H). *anti:* 7.40–7.08 (m, 5H), 6.04–5.47 (m, 1H), 5.23–4.95 (m, 2H), 3.82–3.55 (m, 1H), 2.77 (quint, J = 7 Hz, 1H), 2.40–1.86 (m, 2H), 1.60 (br s, 1H), 1.30 (d, J = 7 Hz, 3H).

1-Phenyl-5-hexen-3-ol. ^{1}H NMR ($CDCl_3$) δ 7.40–7.00 (m, 5H), 6.06–5.61 (m, 1H), 5.30–5.00 (m, 2H), 3.69 (quint, J = 5 Hz, 1H), 3.10–2.60 (m, 2H), 2.34–2.15 (m, 2H), 1.91–1.65 (m, 2H), 1.61 (s, 1H).

2-Phenyl-4-penten-2-ol. ^{1}H NMR ($CDCl_3$) δ 7.52–7.18 (m, 5H), 5.88–5.41 (m, 1H), 5.25–4.98 (m, 2H), 2.82–2.37 (m, 2H), 2.03 (br s, 1H), 1.55 (s, 3H).

2-Methyl-1-(4-nitrophenyl)-3-buten-1-ol. ^{1}H NMR ($CDCl_3$) δ *anti:* 8.22–8.20 (m, 2H), 7.52–7.48

(m, 2H), 5.83–5.70 (m, 1H), 5.34–5.07 (m, 2H), 4.52 (d, J = 5 Hz, 1H), 2.50–2.28 (m, 1H), 2.28 (br s, 1H), 0.94 (d, J = 7 Hz, 3H). *syn:* 8.22–8.20 (m, 2H), 7.52–7.48 (m, 2H), 5.83–5.70 (m, 1H), 5.34–5.07 (m, 2H), 4.66 (d, J = 6 Hz, 1H), 2.63–2.58 (m, 1H), 2.06 (br s, 1H), 0.96 (d, J = 7 Hz, 3H).

1-(4-Chlorophenyl)-2-methyl-3-buten-1-ol. ^{1}H NMR ($CDCl_3$) δ *anti:* 7.33–7.23 (m, 4H), 5.81–5.70 (m, 1H), 5.23–5.19 (m, 2H), 4.35–4.33 (m, 1H), 2.58–2.53 (m, 1H), 1.61 (br s, 1H), 0.87 (d, J = 7 Hz, 3H). *syn:* 7.33–7.23 (m, 4H), 5.81–5.70 (m, 1H), 5.10–5.04 (m, 2H), 4.63–4.60 (m, 1H), 2.83–2.78 (m, 1H), 1.97 (br s, 1H), 0.98 (d, J = 7 Hz, 3H).

2-Methyl-1-phenyl-3-buten-1-ol [20]. ^{1}H NMR ($CDCl_3$) δ *anti:* 7.37–7.24 (m, 5H), 5.86–5.74 (m, 1H), 5.23–5.18 (m, 2H), 4.36 (d, J = 8 Hz, 1H), 2.53–2.44 (m, 1H), 2.13 (br s, 1H), 0.87 (d, J = 7 Hz, 3H). *syn:* 7.37–7.24 (m, 5H), 5.86–5.74 (m, 1H), 5.09–5.04 (m, 2H), 4.63 (d, J = 6 Hz, 1H), 2.62–2.57 (m, 1H), 1.91 (br s, 1H), 1.01 (d, J = 7 Hz, 3H).

1-(4-Methoxyphenyl)-2-methyl-3-buten-1-ol. ^{1}H NMR ($CDCl_3$) δ *anti:* 7.19 (d, J = 8 Hz, 2H), 6.81 (d, J = 8 Hz, 2H), 5.76–5.62 (m, 1H), 5.16–5.10 (m, 1H), 4.99–4.95 (m, 1H), 4.23 (d, J = 8 Hz, 1H), 3.74 (s, 3H), 2.41–2.35 (m, 1H), 2.03 (br s, 1H), 0.77 (d, J = 7 Hz, 3H). *syn:* 7.15 (d, J = 8 Hz, 2H), 6.80 (d, J = 8 Hz, 2H), 5.76–5.62 (m, 1H), 5.16–5.10 (m, 1H), 4.99–4.95 (m, 1H), 4.48 (d, J = 8 Hz, 1H), 3.74 (s, 3H), 2.51–2.46 (m, 1H), 1.79 (br s, 1H), 0.95 (d, J = 7 Hz, 3H).

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REFERENCES

[1] (a) For recent leading reviews see: Yamamoto, Y.; Asao, N. Chem Rev 1993, 93, 2207–2293; (b) Roush, W. R. In Comprehensive Organic Synthesis; Trost, B. M., Ed.; Pergamon: Oxford, 1990; Vol. 2, pp 1–53, and references cited therein.

[2] (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. J Am Chem Soc 1980, 102, 7107; (b) Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. Tetrahedron 1984, 40, 2239. (c) For reviews on allyltin reagents see: Pereyre, M.; Quintard, J.-N.; Rahm, A. Tin in Organic Synthesis; Butterworths: London, 1987; (d) Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. Tetrahedron 1993, 49, 7395.

[3] Marshall, J. A. Chem Rev 1996, 96, 31.

[4] (a) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. J Am Chem Soc 1993, 115, 7001; (b) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. J Am Chem Soc 1993, 115, 8467.

[5] (a) Kira, M.; Sato, K.; Sakurai, H. J Am Chem Soc 1988, 110, 4599; (b) Kira, M.; Sato, K.; Sakurai, H. J Am Chem Soc 1990, 112, 257.

[6] (a) Hosomi, A.; Kohra, S.; Tominaga, Y. J Chem Soc Chem Commun 1987, 1517; (b) Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. J Org Chem 1990, 55, 2415. (c) For a review see, Hosomi, A. Rev Heteroatom Chem 1992, 7, 214.

[7] (a) Kobayashi, S.; Nishio, K. Tetrahedron Lett 1993, 34, 3453; (b) Kobayashi, S.; Nishio, K. J Org Chem 1994, 59, 6620.

[8] (a) Gingras, M. Tetrahedron Lett 1991, 32, 7381–7384; (b) Brigaud, T.; Doussot, P.; Portella, C. J Chem Soc Chem Commun 1994, 2117.

[9] Martínez, A. G.; Barcina, J. O.; Heras, M. d. R. C.; Cerezo, Á. d. F. Org Lett 2000, 2, 1377, and references cited therein.

[10] (a) Boldrini, G. P.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. J Chem Soc Chem Commun 1986, 685; (b) Boldrini, G. P.; Lodi, L.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. J Org Chem 1987, 52, 5447.

[11] (a) Nishida, M.; Tozawa, T.; Yamada, K.; Mukaiyama, T. Chem Lett 1996, 1125; (b) Yamada, K.; Tozawa, T.; Nishida, M.; Mukaiyama, T. Bull Chem Soc Jpn 1997, 70, 2301.

[12] (a) Akiba, K.-y.; Ito, Y.; Kondo, F.; Ohashi, N.; Sakaguchi, A.; Kojima, S.; Yamamoto, Y. Chem Lett 1992, 1562; (b) Yamamoto, Y.; Sakaguchi, A.; Ohashi, N.; Akiba, K.-y. J Organomet Chem 1996, 506, 259.

[13] Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. J Org Chem 1981, 46, 1049.

[14] Fishwick, M.; Wallbridge, M. G. H. J Organomet Chem 1970, 25, 69.

[15] Auge, J.; Bourleaux, G. J Organomet Chem 1989, 377, 205.

[16] Wrackmeyer, B. Ann Rep NMR Spectroscopy 1985, 16, 73.

[17] (a) For example see: Ross, M. R.; Martin, J. C. J Am Chem Soc 1981, 103, 1234; (b) Kojima, S.; Kajiyama, K.; Nakamoto, M.; Akiba, K.-y. J Am Chem Soc 1996, 118, 12866; (c) Kojima, S.; Doi, Y.; Okuda, M.; Akiba, K.-y. Organometallics 1995, 14, 1928.

[18] Based upon the signal separation of 38 Hz (^{19}F NMR) for the two sets of signals. For example see: Becker, E. D. High Resolution NMR Theory and Chemical Applications, 2nd ed; Academic Press: New York, 1980, Chapter 11.3.

[19] Heathcock, C. H.; Kiyooka, S.-i.; Blumenkopf, T. A. J Org Chem 1984, 49, 4214.

[20] Yamamoto, Y.; Yatagai, H.; Maruyama, K. J Am Chem Soc 1981, 103, 1969.