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NMR STUDY ON TRANSMETALLATION REACTION BETWEEN ALLYLTINS AND $SnCl_4$

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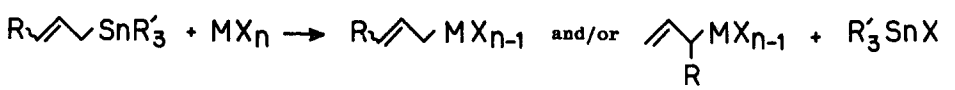
Abstract: Various allyltrialkyltins react with a typical Lewis acid, $SnCl_4$, at -50 °C. The tin compounds with a less substituted allyl group immediately and cleanly give the corresponding allyltrichlorotins via transmetallation through S_E2' pathway, while more substituted ones give precipitates. Crotyltributyltin and $SnCl_4$ first afford (1-methylallyl)trichlorotin, which then isomerizes to crotyltrichlorotin. Electron deficiency of the pentadienyl moiety in pentadienyltrichlorotin is evident as is the case with allyltrichlorotins. Highly fluxional structure of (Z)-pentadienyltrichlorotins is revealed. Interaction between some allyltins and $BF_3 \cdot OEt_2$ is also demonstrated.

Introduction

Allyltrialkyltin compounds are often utilized in synthetic chemistry as useful C-C bond forming reagents by means of various methods; e.g. thermal, high-pressure-promoted, Lewis acid-promoted, transition metal-catalyzed, photochemical, radical reactions, and so forth.[1] Among them, one of the most familiar is Lewis acid-promoted addition to carbonyl compounds, where the role of the Lewis acid is generally accepted as activation of the carbonyl compound by its coordination to the carbonyl oxygen atom.[2] In this instance, the actually reacting species is allyltrialkyltin itself. In addition, several workers including ourselves have recently indicated that allyl-, crotyl-, and pentadienyltrialkyltins first react with a Lewis acid,[3,4] such as $SnCl_4$,[3a-d,4] $BuSnCl_3$,[3e] Bu_2SnCl_2,[3f,g] AlX_3,[3h] $TiCl_4$,[3c,i] and $FeBr_3$[3j], to form a reactive species, which is considered to be allylmetal halide formed by transmetallation reaction (Scheme 1).

Scheme 1.



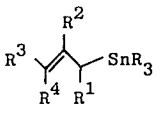
Such allylmetal halides are interesting in their reactivity and selectivity,[3] which are different from those of the parent allyltrialkyltin. As one of the most effective synthetic applications of the transmetallation, pentadienyltrichlorotin was used to introduce a pentadienyl group to an acylquinone without undergoing Diels-Alder reaction.[3a,b] In the

crotyl system, the regio- and stereochemical aspects are associated with regio- and diastereoselectivity.[3c,e-j] Nonetheless, only a few studies about the feature of such transmetallation reaction have been made.[3g] We, therefore, studied the reaction between various allyltrialkyltins and Lewis acids, especially $SnCl_4$ as a typical case by means of NMR spectroscopy. In the system of allyltrialkyltin-$SnCl_4$, the generality, the limitation, and the reaction mode of the transmetallation were made evident.

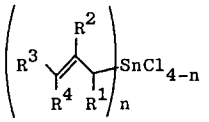
Results and Discussion

Table I shows ^1H and ^{119}Sn NMR chemical shifts and coupling constants between H^1 and Sn of a series of allylchlorotins (n=1-4), each of which was given by the reaction between tetraallyltin and an appropriate amount of $SnCl_4$ in $CDCl_3$ at room temperature.[5] The most characteristics are chemical shifts of H^1 and coupling constants between H^1 and Sn. These were useful for the diagnosis of the reaction including more complex tin reagents.

The allyltrialkyltins (**1a-l**, **5**)[6] applied to this study and the product allylchlorotins (**2-4**) are shown below.



1a-i R=*n*-Bu, **1j-l** R=Me

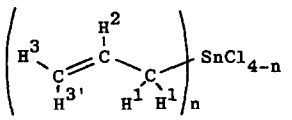


2 n=1, **3** n=2, **4** n=3, **5** n=4

	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
a	H	H	H	H	**h**	H	H	Ph	H
b	Me	H	H	H	**i**	H	CH=CHCH=CH		H
c	H	Me	H	H	**j**	H	H	$CH=CH_2$,H	
d	H	H	Me,H		**k**	H	H	CH=CHMe,H	
e	Me	H	Me,H		**l**	H	Me	H	$CH=CH_2$
f	H	Me	Me,H		**m**	H	H	$CMe=CH_2$,H	
g	H	H	Me	Me					

Generality and Limitation of the Transmetallation of Allyltins and $SnCl_4$. We first surveyed the transmetallation reaction with excess amount (2 equiv to **1**) of $SnCl_4$ at -50 °C in $CDCl_3$-CCl_4 and found many of applied allyltins (**1a-d**, **f**, **i**, **j** and **l**) immediately and cleanly gave the corresponding allyltrichlorotins (**2a-d**, **f**, **i**, **j**, **l** and **m**) as indicated in Table II. By comparison of the NMR data (mainly δ_{H^1} and J_{Sn-H^1}) in Table II with those in Table I, the newly formed allyltin compounds were identified as **2** without exception. No highly allylated chlorotin compounds such as **3** were detected. Each allyltrichlorotin characteristically has a chemical shift of H^1 in 3.1-3.7 ppm and a coupling constant between H^1 and Sn in 104-122 Hz.

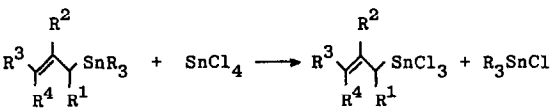
Table I. NMR data of $(C_3H_5)_nSnCl_{4-n}$ (n=1-4)[a]



Compound	n	^1H chemical shift/δ ppm[b]				J_{Sn-H^1}/Hz	^{119}Sn chemical shift/δ ppm[c]
		H^1	H^2	H^3	$H^{3'}$		
2a	1	3.14	5.96	5.35	5.42	121	-28
3a	2	2.70	5.94	5.12	5.20	81	46
4a	3	2.29	5.93	4.92	5.02	69	58
5a	4	1.91	5.92	4.72	4.86	63	-48

[a] NMR measurement was performed in $CDCl_3$ at room temperature. [b] Relative to $CHCl_3$ (δ 7.26). [c] Relative to Me_4Sn (δ 0.00).

Table II. Reaction of **1** with $SnCl_4$[a]



1 **2**

1 (*E*/*Z*)	**2** (*E*/*Z*)	δ_{H1} of **2**/ ppm (J_{Sn-H1}/ Hz)
a	**a**	3.22 (119)
b and **d**[b]	**d** (4/6)	(*E*)-**2d**:3.20 (109); (*Z*)-**2d**:3.25 (117)
c	**c**	3.18 (113, 117)
d (1/2)	**d** (4/6)[c]	(*E*)-**2d**:3.20 (109); (*Z*)-**2d**:3.25 (117)
e (>9/1)	-[d]	-
f (4/6)	**f** (4/6)	(*E*)-**2f**:3.13 (115); (*Z*)-**2f**:3.15 (104)
g	-[d]	-
h	-[d]	-
i	**i**	3.72 (105, 109)
j (8/2)	**j** (8.5/1.5)[c]	(*E*)-**2j**:3.22 (122); (*Z*)-**2j**:4.33 (82)
k[e]	-[d]	-
l (<1/9)	**l** and **m**[c]	(*E*)-**2l**:3.28 (115); (*Z*)-**2l**:3.32 (119); (*E*)-**2m**:3.33 (119)

[a] NMR spectra were observed at -50 °C in $CDCl_3$-CCl_4. [b] **1b**/**1d** = 1/1. [c] Isomeric ratio depends on the reaction conditions applied. For detailed discussion, see Tables III and V, Fig.1 and the text. [d] Precipitates were formed and well-resolved NMR spectra were not obtained. [e] Stereoisomeric mixture.

In the reaction of **1a** as the simplest instance, ^{119}Sn NMR signals of the products appeared at -28 ppm and 157 ppm at room temperature; the former agrees with **2a** in Table I and the latter corresponds to Bu_3SnCl concomitantly formed according to Scheme 1($MX_n=SnCl_4$).

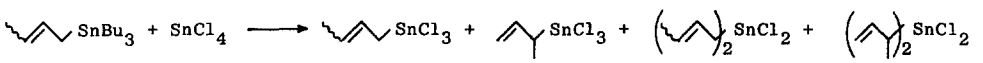
Allyltrialkyltins, **1e, g, h** and **k**, and $SnCl_4$, however, gave precipitates instantly. Therefore, no well-resolved NMR spectra were obtained. Although the precipitates have not been characterized well, they would form by cationic polymerization as is the case with olefins,[7] since such allyltins have a substituent at the odd-numbered position of the allyl or pentadienyl moiety as to stabilize the allyl cation. On the other hand, **1f** and **1l** have a substituent at the even-numbered position where there is no contribution to the allylic conjugation to stabilize the cation.

Crotyltin and $SnCl_4$. Among transmetallation reactions of allyltins, crotyltin is of our particular interest in its regio- and stereochemistry. Our investigation of the transmetallation between crotyltin **1d** and $SnCl_4$ revealed the reaction mode and the complexity of the isomerization between (*E*)-**2d**, (*Z*)-**2d**, and **2b**.

We observed the clean and immediate formation of crotyltrichlorotin **2d** in the reaction between **1d** and $SnCl_4$ even at -50 °C or lower temperature,[8] though Keck and his co-workers have reported the formation of **2d** at 23 °C.[3c] In addition, we also confirmed the concomitant formation of (1-methylallyl)trichlorotin **2b**, dicrotyldichlorotin **3d**,[9] and di(1-methylallyl)dichlorotin **3b**[9] depending on the amount of added $SnCl_4$ and the reaction time.

Table III shows the results of the transmetallation with various amounts of $SnCl_4$ in $CDCl_3$-CCl_4 at -50 °C. All products were identified by ^1H NMR spectra according to the criterion mentioned above. The product ratio was determined after 5-10 min from the addition of $SnCl_4$ solution in CCl_4 to **1d** (*E*/*Z*=1/2) in $CDCl_3$.

Table III. Transmetallation between **1d** and $SnCl_4$ at -50 °C

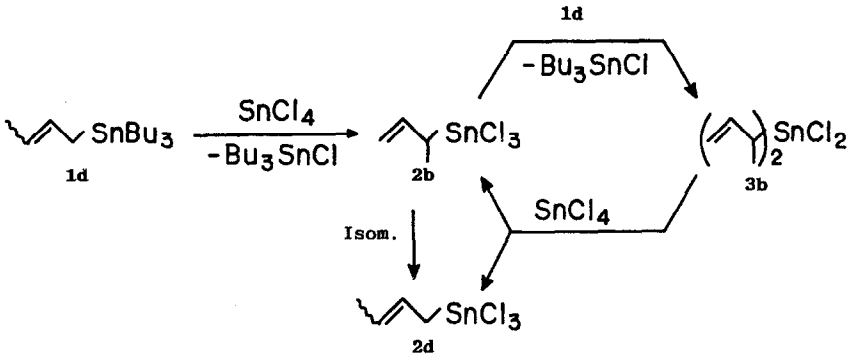


1d (*E*/*Z*=1/2) **2d** **2b** **3d** **3b**

Run	$[SnCl_4]/[1d]$	Product ratio[a] / %				
		(*E*)-**2d**	(*Z*)-**2d**	**2b**	**3d**	**3b**
1	0.5	0	0	0	16[c]	84
2	0.5+0.5[b]	14	58	23	5[c]	0
3	1.0	18	27	55	trace	0
4	1.2	17	36	47	0	0
5	1.7	25	31	44	0	0
6	3.0	44	44	12	0	0

[a] Determined by ^1H NMR at -50 °C after 5-10 min from the addition of $SnCl_4$. The ratio is based on the amount of the butenyl (C_4H_7) residues. [b] To the sample in run 1 was added more 0.5 equiv of $SnCl_4$. [c] *E*/*Z*=ca.1/2.

Scheme 2.

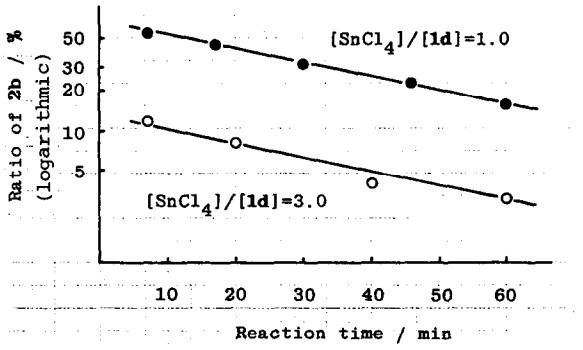


When 0.5 equiv of $SnCl_4$ to **1d** was added, only **3b** and **3d** were detected (run 1). On the other hand, the addition of an equivalent or excess amount of $SnCl_4$ to **1d** afforded mono-transmetalated **2b** and **2d** exclusively (runs 2-6). The high selectivity in producing **2** or **3** is considered to be due to their thermodynamic stability, though just an equivalent of $SnCl_4$ to **1d** is sufficient to consume **3** (runs 2 and 3).

It is noteworthy that in run 1 in Table III the allyl-rearranged 1-methylallyl species **3b** was the major product. This means the transmetallation reaction mainly proceeds through an S_E2' pathway, which is also supported by the experiments in runs 3-5 where the major part of the transmetalated products was also allyl-rearranged **2b** according to the first step in Scheme 2. The rapid formation of **2b** at the initial stage of the transmetallation causes the formation of the α-adduct along with the normal γ-adduct in the $SnCl_4$-mediated reaction between **1d** and an aldehyde by competing with the carbonyl activation as Keck indicated.[3c]

We also observed that initially formed **2b** gradually isomerized to **2d** at -50 °C (Fig. 1). As far as Fig. 1 indicates, contribution of the $SnCl_4$-mediated intermolecular isomerization is small under the present conditions and we can conclude the main isomerization pathway is intramolecular one through [1,3] migration of the $SnCl_3$ moiety, because the rate of isomerization was almost the same regardless of the amount of added $SnCl_4$.

Fig. 1. Isomerization of **2b** to **2d** at -50 °C



Although the isomerized **2d** kinetically favored the (Z)-conformation slightly (E/Z=1/1-4/6), thermodynamically (E)-**2d** was preferred; E/Z ratios of all samples in runs 2-6 were different just after mixing, but became the uniform one, E/Z=2/1, after standing overnight at room temperature.[20]

The time-dependency of the product ratio described above is similarly observed in the reaction of **1d** and Bu_2SnCl_2 by Tagliavini and his co-workers.[3g] Thus, the nature of the two systems is similar. The reaction with $SnCl_4$, however, is about a hundred times faster than that of with Bu_2SnCl_2, because of the stronger Lewis acidity of $SnCl_4$.

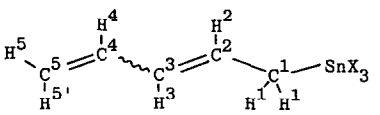
2,4-Pentadienyltins (PDTs) and $SnCl_4$. Another important and interesting transmetallation is that of PDTs and $SnCl_4$. We have already reported this reaction in the anthracyclinone synthesis,[3a,b] where the resulting trichloro-PDT (**2j**) is utilized as a highly selective reagent for the (E)-pentadienyl group-transfer to an acylquinone via Michael addition, while trimethyl-PDT (**1j**) also brings about a considerable amount of the Diels-Alder adduct.

We, here, reveal the structural and electronic feature of **2j** given by the transmetallation. We also demonstrate the transmetallation between $SnCl_4$ and (2-methylpentadienyl)trimethyltin (**1l**) which has an unsymmetrically substituted pentadienyl group.

Transmetallation of PDT **1j** (E/Z=78/22) at -50 °C also proceeded immediately to give the corresponding pentadienylchlorotins, (E)-**2j**, (Z)-**2j**, and **3j**, which were identified by ^1H, ^{13}C, and ^{119}Sn NMR. The NMR data of **2j** were summarized in Table IV in comparison with those of **1j**.

As can be readily seen, the chemical-shift values of the odd-numbered H and C of (E)-**2j**

Table IV. NMR data of **1j** and **2j**[a]



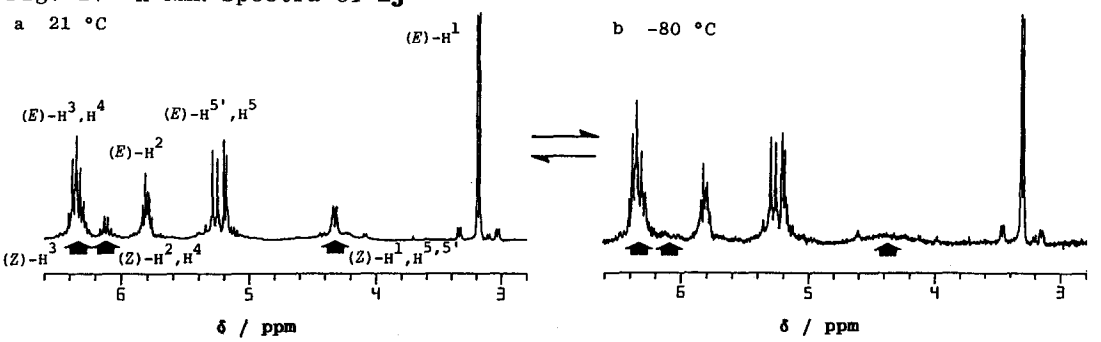
X		^1H NMR / δ ppm (δ_{2j}-δ_{1j})						J_{Sn-H^1}
		H^1	H^2	H^3	H^4	H^5	$H^{5'}$	Hz
Me	(*E*)-**1j**	1.81	5.84	5.91	6.28	4.79	4.94	68
Cl	(*E*)-**2j**	3.22(1.41)	5.79(-0.05)	6.35(0.44)	6.30(0.02)	5.19(0.40)	5.27(0.33)	122
Cl	(*Z*)-**2j**	4.33	6.10	6.3-6.4[b]	6.10	4.33		82

X		^{13}C NMR / δ ppm (δ_{2j}-δ_{1j})					^{119}Sn NMR
		C^1	C^2	C^3	C^4	C^5	δ ppm
Me	(*E*)-**1j**	17.1	126.9	134.6	137.5	111.4	0.7
Cl	(*E*)-**2j**	36.1(19.0)	121.5(-5.4)	137.2(2.6)	135.2(-2.3)	119.0(7.6)	-43
Cl	(*Z*)-**2j**	77.1	124.3	134.6	124.3	77.1	-[c]

[a] Observed at room temperature. [b] Overlapped. [c] Not observed.

moved to low field compared with those of (E)-1j as observed in the case of allyltrichlorotin.[10] This means that the electron density decreased[11] at the odd-numbered position of the pentadienyl moiety of 2j owing to the electron-withdrawing character of the substituted trichlorotin group and the hyperconjugative mesomeric effect. The electron deficiency of 2j is thought to be a reason for its low reactivity[3a,b] toward Diels-Alder reaction as mentioned above.

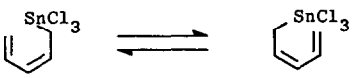
Fig. 2. ^1H NMR spectra of **2j**[a,b]



[a] The peaks belonging to (Z)-2j are indicated by arrows. [b] Observed in $CDCl_3$-$CFCl_3$.

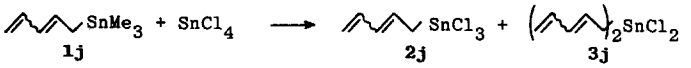
One more interesting feature of 2j is the structure of the minor transmetalated product, (Z)-2j. On ^1H and ^{13}C NMR were observed only three distinguishable protons or carbons (δ 4.33, 6.10, and 6.3-6.4 on ^1H NMR and δ 77.1, 124.3, and 134.6 on ^{13}C NMR) which supposedly belonged to (Z)-2j (Fig. 2a and Table IV). These peaks had the following characteristics. (1) NMR decoupling experiments confirmed that these peaks couple each other; irradiation at 4.33 ppm converted the quartet at 6.10 ppm to a doublet and irradiation at 6.35 ppm did it to a triplet. (2) The ratio of the peak area was 4:2:1 from high field to low field. (3) The chemical shifts were about the means of the corresponding shifts of (E)-2j, e.g. the chemical shift of H^2 and H^4 of (Z)-2j (δ 6.10) is close to the average of those of (E)-2j (δ 6.05). (4) The peaks broadened reversibly at a low temperature while those of (E)-2j remained sharp (Fig. 2).

These peculiar features are fully explained in terms of the fluxionality[12] of (Z)-2j. Rapid [1,5] sigmatropic migration of trichlorotin group occurs within the NMR time scale.



In the present experiment, the exact coalescence temperature (T_C) was not obtained, but T_C < 173 K. Using the T_C value thus evaluated, the free enthalpy of activation $\Delta G^{\ddagger}$ of the [1,5] migration can be estimated; $\Delta G^{\ddagger}$ < 7.4 kcal/mol,[13] which is much smaller than that of a similar system, (Z)-pentadienyltriphenyltin (19.4 kcal/mol)[12a] and comparable to that of a cyclic system, cyclopentadienyltrimethyltin (7.1 kcal/mol).[12b]

Table V. Transmetallation between **1j** and $SnCl_4$ at -50 °C



1j **2j** **3j**

Run	$[SnCl_4]/[1j]$	Product ratio[a] / %		
		(*E*)-2j	(*Z*)-2j	3j[b]
1	1.0	60	11	29
2	2.0	85	15	0
3	4.0	92	8	0
4	> 6.0	96	4	0

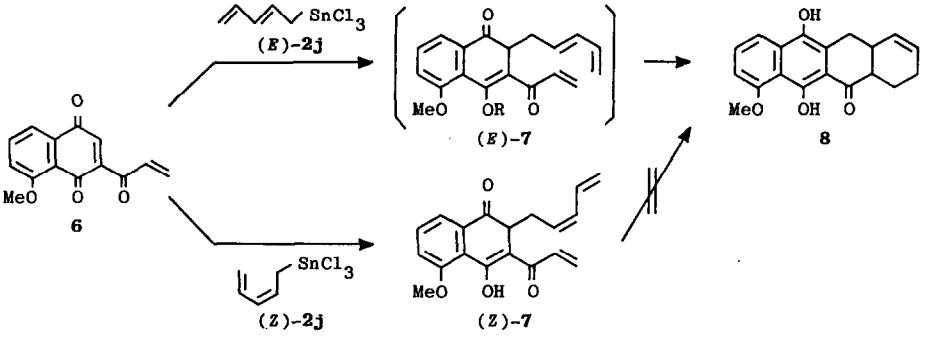
[a] Determined by ^1H NMR at -50 °C. The ratio is based on the amount of the pentadienyl residue. [b] Stereoisomeric ratio was not determined.

The PDT product ratio at -50 °C varied with the amount of added $SnCl_4$ and is summarized in Table V. Just after mixing, ca. 45 % of 3j was detected in run 1 and even in runs 2 and 3, ca. 10 % of 3j was also observed. Since this transmetallation includes a slow process, i.e. 3j + $SnCl_4$ → 2 2j , and it takes several minutes for the reaction to complete, the NMR measurement was performed after the mixture standing for 30 min at -50 °C. The ratio remained unchanged after an hour at the same temperarure, and clean and highly (E)-selective transmetallation was observed in the presence of an excess amount of $SnCl_4$.

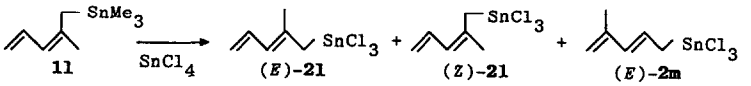
It was found that the E/Z ratio of 2j was determined kinetically: when $SnCl_4$ was added to 1j at a time, the ratio of (E)-2j increased with the increase of the amount of $SnCl_4$ as shown in Table V. But when to the sample in run 2 was added additional 2 equiv of $SnCl_4$ at -50 °C, the E/Z ratio did not increase but remained 85/15. In addition, in run 4, when the temperature was raised to 15 °C from -50 °C, the E/Z ratio decreased irreversibly to 82/18 from 96/4, i.e. re-cooling of the sample to -50 °C did not improve the ratio. The interconversion between (E)- and (Z)-2j seemed to be rather slow especially at a low temperature.

The observed isomeric ratio of 2j affects the product selectivity in the tandem Michael/Diels-Alder reaction with the acryloylquinone 6,[3a,b] which gives the tetracyclic compound 8 as the major product presumably via intramolecular [4+2] cycloaddition of the dienylated product (E)-7 (Scheme 3). This reaction, however, formed the uncyclized compound (Z)-7 as a side product, the yield of which depended on the amount of $SnCl_4$ used. When the amount of $SnCl_4$ added was increased from 1.2 to 6.0 equiv to 1j, the product ratio of 8 was increased from 76 to 94 %. This result is almost parallel to the ratio, (E)-/(Z)-2j in Table V. As recognized from its rapid [1,5] migration, (Z)-2j most probably takes s-cis conformation which would result in the formation of (Z)-pentadienylated product, (Z)-7. It is unable to cyclize intramolecularly and remains intact. Conclusively, the characteristics of this transmetallation and PDT are reflected in the tandem reaction of the acryloylquinone.

Scheme 3.



When unsymmetrically substituted PDT **11** was applied to the transmetallation reaction with $SnCl_4$, the regiochemical factor also came into question. Combinaton of PDT **11** and 2 equiv of $SnCl_4$ at -50 °C afforded a mixture of (E)-**21**, (Z)-**21**, and (E)-**2m**, of which the structures were assigned by ^1H NMR, in the ratio 14:26:60 respectively. The



observed isomeric ratio can be understood to be simply affected by the steric hindrance of the methyl substituent on the pentadienyl moiety. No detection of (Z)-**2m** denotes the fluxionality of (Z)-PDT and the thermodynamic stability of (Z)-**21**.[14] The fluxionality was also indicated by the fact that the two protons at the 5-position of (Z)-**21** were undistinguishable by NMR spectroscopy even at -50 °C.

Reaction between **1** and $BF_3 \cdot OEt_2$. NMR study of the reaction between **1d** and $BF_3 \cdot OEt_2$ as another typical Lewis acid in $CDCl_3$ provided no evidence of transmetallation. Only moderate broadening of the peaks of **1d** was observed by ^1H NMR. This observation is concomitant with that by Denmark and his co-workers in the allyltin-$BF_3 \cdot OEt_2$ system.[4] We, therefore, also estimate that $BF_3 \cdot OEt_2$ can weaken the C-Sn bond of **1d** by interacting with it and catalyze [1,3] shift of the Bu_3Sn group but cannot undergo the transmetallation to give allylic boron compounds. This aspect is not in conflict with the product analysis in the **1d**-$BF_3 \cdot OEt_2$-aldehyde reaction system reported by Tagliavini and his co-workers.[3g]

In addition, $BF_3 \cdot OEt_2$ did not yield precipitates in the reaction with **1h**. Indeed, almost no reaction occurred. This fact indicates the interaction between allyltin **1** and

$BF_3 \cdot OEt_2$ is weaker than that between **1** and $SnCl_4$. The polymerization of **1** may relate the oxidative character of $SnCl_4$.[15]

Conclusion

Generality and limitation in the transmetallation reaction between allyltins **1** and $SnCl_4$ were revealed; allytins with a less substituted allyl group underwent the reaction immediately and cleanly even at -50 °C or probably at lower temperature while more substituted ones as to stabilize the cation afforded precipitates instantaneously. The reactions of crotyltin **1d** and PDTs **1j** and **1l** were especially interesting in their regio- and stereochemistry, and it was concluded that the transmetallation proceeded mainly via S_E2' pathway and then, particularly in the reaction of **1d**, migration the $SnCl_3$ group gradually followed to result in the isomerization of **2b** to **2d**. The reaction path via diallyldichlorotin **3** and the isomerization from (Z)-**2d** to (E)-**2d** were also present, thus the whole reaction was of some complexity. This makes the reaction between **1d** and an aldehyde in the presence of $SnCl_4$ complex one. In the case of PDTs, **2j** as well as other transmetalated **2** was proved of its electron-deficiency, which can explain its reactivity toward acylquinones. A minor product (Z)-**2j** had an interesting structural feature; very rapid [1,5] shift of $SnCl_3$ group was observed and this is a good example clearly indicating the fluxionality of (Z)-PDT compounds. Unsymmetrically substituted PDT **1l** afforded S_E2' product **2m** as the major product presumably owing to the steric effect of the methyl substituent. Another typical Lewis acid, $BF_3 \cdot OEt_2$, showed a weaker interaction with allyltins **1** than $SnCl_4$. However, it seemed to catalyze [1,3] shift of Bu_3Sn group in allyl systems.

All the features revealed here in the reaction between allyltins and $SnCl_4$ or $BF_3 \cdot OEt_2$ will be representative for the reaction of other Lewis acids. We, therefore, should be careful in dealing with reaction of an allyltin, which is stable but has a rather weak and reactive C-Sn bond[16] contributing to its diverse reactivity including the transmetallation.

Experimental

General. NMR spectra were obtained on a JEOL JNM-FX400 spectrometer (399.8 MHz for ^1H, 100.5 MHz for ^{13}C, 149.1 MHz for ^{119}Sn). Chemical shifts are reported as δ values in ppm relative to $CHCl_3$ (δ 7.26) for ^1H, $CDCl_3$ (δ 76.85) for ^{13}C, and tetramethyltin (δ 0.00) for ^{119}Sn. Coupling constants (J) are reported in Hz. All solvents for NMR ($CDCl_3$, CCl_4, and $CFCl_3$) were used without further purification after purchasing. Lewis acids, $SnCl_4$ and $BF_3 \cdot OEt_2$, were used as 1 M solutions in $CDCl_3$ or CCl_4. Allyltributyltins **1a-d,f-i** were synthesized according to the literature.[6] Allyltin **1e** was synthesized from 2-chloro-3-pentene and n-Bu_3SnLi.[17] Dienyltins **1j** and **k** were synthesized in a similar manner to the literature method.[18] (2-Methylpentadienyl)tin **1l** was synthesized from 2-methylpentadienylpotassium and Me_3SnBr in THF.[3b,19]

Reaction between tetraallyltin and $SnCl_4$. (Table I) ^1H NMR measurement: To a $CDCl_3$ solution (0.5 ml) of tetraallyltin (**5a**; 34 mg; 0.12 mmol) in an NMR sample tube (5 mmϕ) was added a $CDCl_3$ solution of $SnCl_4$ (1 M; 0.04 ml) by a syringe at room temperature under N_2. From ^1H NMR measurement at room temperature, triallylchlorotin **4a** as the major product was detected along with diallyldichlorotin **3a** and tetraallyltin **5a**.

Both **3a** and **2a** were also prepared similarly as the sole product using 0.12 mmol and 0.5

mmol of $SnCl_4$ respectively.

^{119}Sn NMR measurement was performed in a similar manner using double sample tubes (10 mmϕ). A $CDCl_3$ solution of tetramethyltin as the reference compound was in the inner tube and a mixture of **5a** and $SnCl_4$ in $CDCl_3$ was in the outer tube, since tetramethyltin and $SnCl_4$ react readily.

Reaction between allyltrialkyltins (1) and $SnCl_4$ at -50 °C. (Tables II, III, V, Fig. 1) To a frozen $CDCl_3$ solution (0.5 ml) of an allyltin (1; 0.1 mmol) by liquid N_2 in an NMR sample tube under N_2 was added an appropriate amount of a CCl_4 solution of $SnCl_4$ (1 M) by a syringe through a serum cap over the top of the tube. As soon as the mixture was warmed to melt and react quickly, it was frozen again by liquid N_2. The solidified sample was loaded into the NMR probe at -50 °C, and applied to the measurement at the temperature.

Reaction between pentadienyltin **1j** and $SnCl_4$. (Table IV, Fig. 2) All the NMR measurement appeared in Table IV was performed in a similar manner to that for Table I as mentioned above. The NMR measurement in various temperature shown in Fig.2 was performed as follows. To an ice-cooled solution of **1j** (23 mg; 0.1 mmol) in $CFCl_3$(0.4 ml)-$CDCl_3$(0.2 ml) in an NMR sample tube was added a $CDCl_3$ solution of $SnCl_4$ (1 M; 0.15 ml) by a syringe under N_2 through a serum cap. The temperature of the NMR probe was varied from 21 °C to -100 °C and then up to 21 °C again.

Reaction between 1 and $BF_3 \cdot OEt_2$. This experiment was performed at room temperature in a similar manner to that mentioned above using 1 M $BF_3 \cdot OEt_2$ in CCl_4.

NMR data : chemical shift (integration, multiplicity, coupling constant).

2a: 3.14(2H, d, 8.1, J_{Sn-H}=121), 5.35(1H, d, 9.8), 5.42(1H, d, 16.7), 5.96(1H, ddt, 16.7, 9.8, 8.1).

3a: 2.70(4H, d, 8.6, J_{Sn-H}=81), 5.12(2H, d, 9.8), 5.20(2H, dd, 17.1, 1.3), 5.94(2H, ddt, 17.1, 9.8, 8.6).

4a: 2.29(6H, d, 8.5, J_{Sn-H}=69), 4.92(3H, d, 9.8), 5.02(3H, d, 16.7), 5.93(3H, ddt, 16.7, 9.8, 8.5).

5a: 1.91(8H, d, 8.6, J_{Sn-H}=63), 4.74(4H, dd, 11.1, 1.7), 4.86(4H, dd, 17.1, 1.7), 5.92(4H, ddt, 17.1, 11.1, 8.6).

2b: 1.69(3H, d, 7.5), 2.68(1H, dq, 7.8, 7.5, J_{Sn-H}=121), 5.37(1H, d, 10.0), 5.38(1H, d, 17.0), 6.08(1H, ddd, 17.0, 10.0, 7.8).

3b: 3.17(2H, quintet, 7.3, J_{Sn-H}=73), 5.13(2H, d, 10.1), 5.17(2H, d, 16.8), 6.10(2H, ddd, 16.8, 10.1, 7.3).

2c: 1.88(3H, s, J_{Sn-H}=37), 3.17(2H, s, J_{Sn-H}=113,117), 5.04(1H, d, 1.2, J_{Sn-H}=69), 5.05(1H, br, J_{Sn-H}=78).

(E)-**2d**: 1.74(3H, d, 8.0), 3.19(2H, d, 8.2, J_{Sn-H}=109), 5.55(1H, dq, 15.1, 8.0), 5.86(1H, dt, 15.1, 8.0).

(Z)-**2d**: 1.74(3H, d, 8.6), 3.24(2H, d, 9.2, J_{Sn-H}=117), 5.62(1H, dq, 10.4, 8.6), 5.87(1H, dt, 10.4, 9.2).

(E)-**3d**: 2.68(4H, d, 7.4).

(Z)-**3d**: 2.73(4H, d, 7.6, J_{Sn-H}=75).

(E)-**2f**: ca.1.7(3H), 1.88(3H, s), 3.13(2H, s, J_{Sn-H}=115), 5.56(1H, q, 7.0, J_{Sn-H}=83).

(Z)-**2f**: ca.1.7(3H), 1.80(3H, s), 3.15(2H, s, J_{Sn-H}=104), 5.63(1H, q, 6.4, J_{Sn-H}=81).

2i: 3.72(2H, s, J_{Sn-H}=105,109), 7.34(5H, m).

(E)-**2j**: 3.22(2H, d, 8.2, J_{Sn-H}=122), 5.19(1H, d, 8.9), 5.27(1H, d, 15.9), 5.79(1H, dt, 14.0, 8.2, J_{Sn-H}=69), 6.30(1H, ddd, 15.9, 11.3, 8.9), 6.35(1H, dd, 14.0, 11.3).

(Z)-**2j**: 4.33(4H, d, 11.3, J_{Sn-H}=82), 6.10(2H, q, 11.3), 6.3-6.4 (1H).

3j: 2.82(4H, d, 8.9, J_{Sn-H}=81), 5.06(2H, d, 10.1), 5.15(2H, d, 16.5).

(E)-**2l**: 1.92(3H, s), 3.28(2H, s, J_{Sn-H}=115), 5.20(1H, d, 11.3), 5.27(1H, d, 17.4), 6.14(1H, d, 10.6, J_{Sn-H}=80), 6.53(1H, ddd, 17.4, 11.3, 10.6).

(Z)-**2l**: 1.94(3H, s), 3.32(2H, s, J_{Sn-H}=119), 5.25(2H, d, 13.1, J_{Sn-H}=40), 6.09(1H, d, 11.9, J_{Sn-H}=81), 6.46(1H, dt, 11.9, 13.1).

(E)-**2m**: 1.84(3H, s), 3.33(2H, d, 8.8, J_{Sn-H}=119), 5.03(1H, s, J_{Sn-H}=41), 5.07(1H, s, J_{Sn-H}=46), 5.72(1H, dt, 15.6, 8.8, J_{Sn-H}=61), 6.46(1H, d, 15.6, J_{Sn-H}=78).

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