Tetrahedron Vol. 49, No. 34, pp. 7395-7426, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00
Pergamon Press Ltd

TETRAHEDRON REPORT NUMBER 337

Versatile Roles of Lewis Acids in the Reactions of Allylic Tin Compounds

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(*Received* 6 *October* 1992)

Contents

1. INTRODUCTION

Organotin compounds are widely exploited reagents in organic synthesis.[1] Allylic tin compounds have high σ–π interaction between C=C and C-Sn bonds which makes them more reactive than the corresponding silicon derivatives. In spite of their high reactivity, the tin compounds are stable enough to be isolated and to react at ambient temperature under aerobic conditions. These factors allow them to be applied to various types of reactions, e.g. thermal,[2] high pressure,[3] transition metal-catalyzed,[4] radical,[1g,5] photochemical,[6] tin-lithium exchange reactions,[1c,2a] and so on. The Lewis acid-promoted addition reaction of allylic tin reagents[1,2] to various electrophiles is a popular method for C-C bond formation because of their high reactivity and selectivity.

The first Lewis acid-promoted allylstannation reaction was reported by Maruyama and Naruta in 1978 in their study of quinonoid compounds.[7,8] In 1979, this study was extended to the more general reaction of aldehydes, ketones, and their derivatives.[9,10] Previously, allylic tins were considered to be stable and therefore poorly reactive organometallics toward carbonyl compounds.[11] The ability of allylic tin compounds

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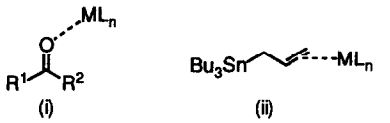
to function as very selective reagents has intrigued many synthetic chemists. Now, a broad approach toward their numerous applications to chemo-, regio-, and stereoselective reactions has been established.[8,9]

Several reviews[1,2] have already appeared describing the development of these selective reactions, but the importance and the influence of the Lewis acid has been insufficiently emphasized. Selectivity in Lewis acid-promoted reactions was highlighted recently.[12] We now review the reactions of allylic tins from the standpoint of the roles of the Lewis acid (ML_n). We can roughly categorize the Lewis-acid promoting reaction in two modes: (i) activation of the substrate, and (ii) activation of the tin reagent (Fig. 1). In this Report, we discuss (i) the Lewis acid activation of the electrophilic substrates by coordination, and then (ii) the reactions and interaction of Lewis acids with allylic tins.

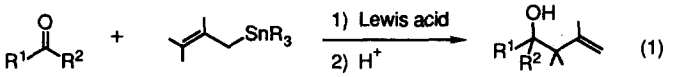
Fig. 1.



2. ACTIVATION OF ELECTROPHILIC SUBSTRATES

2.1. *Simple Coordinative Activation of Carbonyl Compounds*

As the most important and fundamental role, we take up this subject first. Lewis acids can coordinate the heteroatom in electrophiles, mostly carbonyl compounds, and can enhance their electrophilicity. In this section, we review reactions where the Lewis acid simply coordinates and activates the carbonyl group of simple aldehydes and ketones. The Lewis acids are considered not to interact with allylic tins nor any other part of the substrate.



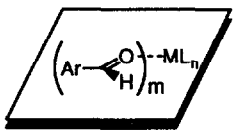
(1)

The first reports on this reaction appeared independently by the Maruyama and Naruta group[9] and by the Sakurai and Hosomi group[10] in 1979. Because allyltin is much less reactive than the corresponding alkali and alkaline earth metal compounds and almost equivalent to the corresponding allylic silane, Lewis acids are essential for the practical reaction of non-activated aldehydes and ketones. The role of the Lewis acid, however, was understood at that time as simple activation of the carbonyl moiety by coordination. Therefore, no detailed and influential function of the Lewis acid was then obvious, although rather high chemoselectivity was reported.[9] The reaction rate decreased in the order of aldehydes>methyl ketones>higher ketones. Similar Lewis acid-induced chemoselectivity, addition to the sterically less congested carbonyl group, was exhibited in comparison with photoreaction (addition to the more conjugated carbonyl group).[13] It is also notable that the Lewis acid-promoted allylstannation allows the coexistence of some labile functional groups.[14-16] In 1980, the reaction was applied to natural product synthesis.[17]

At present, the feature of the interaction (i.e. complexation) between a simple aldehyde and a Lewis acid has been pictured fairly well by several methods. The most direct evidence has been obtained by the X-ray analysis of crystalline aldehyde-Lewis acid complexes[18]; $C_6H_5CHO{\cdot}BF_3$,[19] $(C_6H_5CHO)_2{\cdot}SnCl_4$,[20] and $(p\text{-}t\text{-}BuC_6H_4CHO)_2{\cdot}SnCl_4$.[21] The common feature in these complexes is the coordination of the Lewis acid (BF_3 or $SnCl_4$) to the oxygen atom maintaining *anti*-direction and coplanarity to the aromatic ring. From MNDO calculations,[19a] and *ab initio*[19b,c] caliculations, it was expected that the *anti*-conformation would be more stable than the *syn*-conformation, but the energy difference between the two possible conformations was small, especially for an aliphatic aldehyde. This may affect the reaction path and selectivity in a particular case. Moreover, the activation mechanism of the coordinated carbonyl group was computer-simulated[19,20] by build-up of positive charge and simultaneous lowering of the LUMO energy level at the carbonyl carbon.

Complexation in solution was established by NMR studies (Fig. 2).[18,22-24] The *anti*-conformation of $PhCHO{\cdot}BF_3$ was confirmed by hetero-NOE experiments.[18] Irradiation of the F atom in the complexed BF_3 enhanced the formyl H signal: thus the BF_3 adopts the *syn*-conformation to the formyl H (Scheme 1). Interaction between Lewis acids and carbonyl compounds was also examined by ^{13}C NMR of the formyl carbon and by ^{119}Sn NMR of $SnCl_4$ as the Lewis acid.[22-24] Using the NMR method, the reaction path as well as the mode of coordination can be followed simultaneously. The following three events were identified in the reaction with an aldehyde: (i) equilibrium between an uncomplexed aldehyde, its trimer (trioxane), and aldehyde-Lewis acid complex: (ii) adduct formation with allyltin: and (iii) interaction between a Lewis acid and an allyltin (discussed later) (Scheme 2).[22,23]

Fig. 2.



$ML_n = SnCl_4$: m = 2

BF_3 : m = 1

Scheme 1.

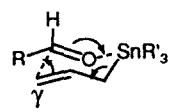
anti-complex *syn*-complex

Scheme 2.

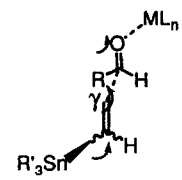
trimer free aldehyde complex

What are the characteristics of the Lewis acid-promoted reaction? This question concerns the reaction mode of the allyltin compound and the transition state. In the simple thermal reaction, it is known that the six-membered cyclic transition state occurs[2,25] where the Lewis acidity of the tin atom is a dominant factor (Fig. 3). When a Lewis acid is present and coordinates with the carbonyl group, then the reaction proceeds via an alternative pathway. An acyclic antiperiplanar[26,27] and *anti*-S_E' path[28] is generally accepted. In ionic reactions, the S_E' path is most probable and this results in γ-selectivity. The radical photoreaction can proceed with opposite regioselectivity.[6b] The weakly Lewis acidic tin atom of trialkylallyltin cannot coordinate to the already occupied carbonyl oxygen atom any more.

Fig. 3.



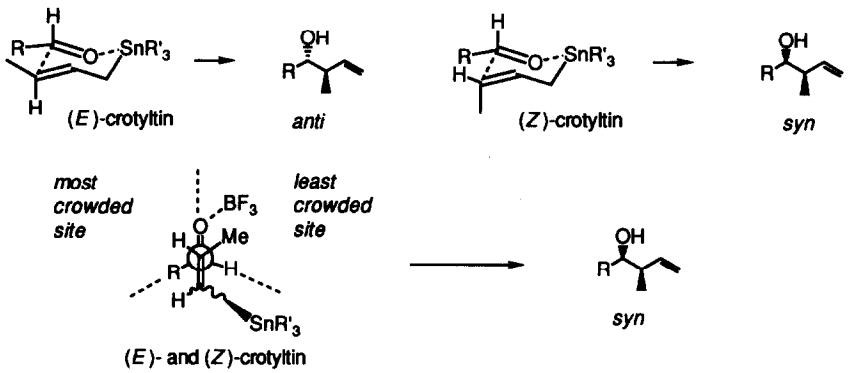
six-membered cyclic transition state



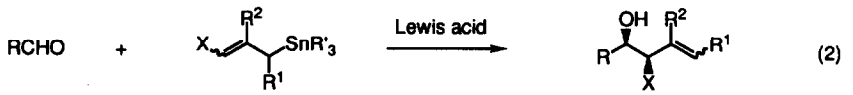
antiperiplanar, anti-S_E' transition state

This mechanistically and synthetically important phenomenon, including the change in the transition state by a Lewis acid, was first reported in the BF_3-promoted reaction of crotyltin (2-butenyltin) by the Maruyama group.[26,29] The remarkable *syn*-(*erythro*-)diastereoselectivity regardless of the double bond geometry of the applied crotyltin was emphasized. This selectivity has been explained by the acyclic transition state where the terminal methyl group of crotyltin occupies the least crowded site around the aldehyde (Scheme 3).[26,27] Similarly, ketones[30,6b] do not undergo a diastereoselective reaction when the two substituents on the carbonyl are sterically almost equivalent. In contrast, the thermal reaction in the absence of any Lewis acid showed diastereoselectivity, *syn* or *anti*, depending on the geometry of the reagent, *Z* or *E*, respectively.[2,27,29-32] Thus, the coordination of a Lewis acid to an aldehyde altered the diastereoisomeric outcome of the (*E*)-crotyltin reaction from exclusive *anti* to exclusive *syn*.[33]

Scheme 3.



After this work,[26] many other reports appeared on the reaction of 3-substituted allyltins which also afforded *syn* alcohol products in preference, though the selectivity varied with the Lewis acids used.[34,35] Longer alkyl,[36-38] alkoxy,[39-41] thioalkoxy,[40] halo,[42] silyl groups[40] and so on[43,44] are substituents at C-3. They are also useful for natural product synthesis.[41,45-46a]

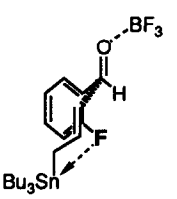


(2)

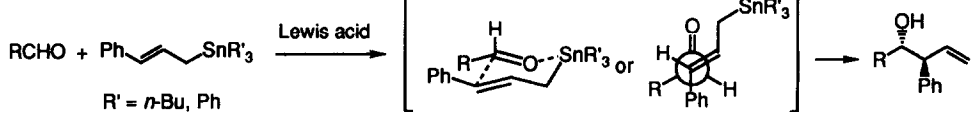
X = *n*-Pr, *n*-Bu, *cyclo*-C_6H_{11}, MeO, EtO, *i*-PrO, *i*-PrS, Cl, Me_3Si, CO_2Et, $ROCH_2CH_2O$, ····
R' = Me, *n*-Bu, Ph

Recently, the acyclic antiperiplanar model was supported by a kinetic study of an aromatic aldehyde-allyltin system.[47] *o*-Halobenzaldehydes exhibited rate enhancement probably owing to the coordination effect of the halogen atom (Cl, F) to the tin, which leads to the antiperiplanar conformation in the transition state (Fig. 4).

Fig. 4.



Scheme 4.

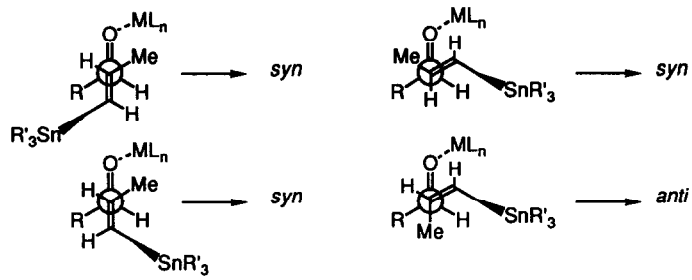


R' = *n*-Bu, Ph

However, cinnamyltin (3-phenylallyltin) exhibited exceptional *anti*-selectivity (Scheme 4).[36] This can be understood by the following scheme. The phenyl group allows the tin atom to become more electropositive so that cinnamyltin favours the cyclic transition state in spite of the presence of Lewis acid coordination.[36,48] Alternatively, this can be explained by an acyclic synclinal transition state. Similar *anti*-selectivity in the presence of $BF_3{\cdot}OEt_2$ was reported in the reaction of (*E*)-crotyldibutylchlorotin.[49] Owing to increased coordinativity of the tin atom, the cyclic transition state was preferred. However, the higher coordinativity of $TiCl_4$ led to the formation of *syn*-products.

Generally, the reaction path via the acyclic transition state is very probable, but an objection against its

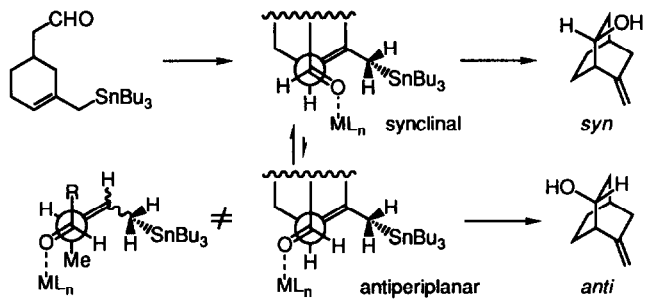
Scheme 5.



antiperiplanar conformation arose. Based on the simple antiperiplanar model, (*Z*)-crotyltin should give products with higher *syn*-selectivity than the (*E*)-isomer (Scheme 5). In practice, the (*E*)-isomer reacted a little faster and with higher *syn*-selectivity.[34] There seems to be a certain contribution of synclinal transition state.[34,50] Similar results were also reported with crotylsilanes.[50]

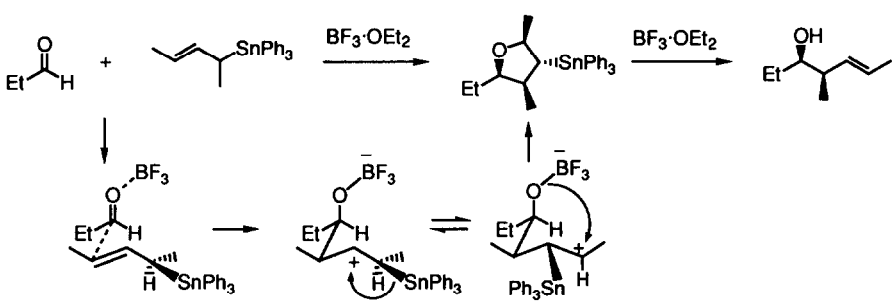
Denmark[51,52] reported, in an *intramolecular* reaction system, that the synclinal conformation was preferred to the antiperiplanar conformation, although the conformation was restricted to one which did not reflect the *intermolecular* reaction system properly (Scheme 6). In the Lewis acid-promoted intramolecular macrocyclizations, a synclinal transition state was also proposed,[53-56] where the stereoselectivity did not necessarily reflect that of intermolecular reactions.[53] The stability of the macrocyclic transition state may influence the selectivity.[55]

Scheme 6.



In a recent report,[57] there was intramolecular capture of an intermediate compound in the BF_3-promoted reaction between propionaldehyde and (1-methylcrotyl)triphenyltin. This product was a stannylated tetrahydrofuran, formed via [1,2] stannyl migration and C-O bond formation (Scheme 7). For efficient ring closure, the synclinal transition state is more plausible.

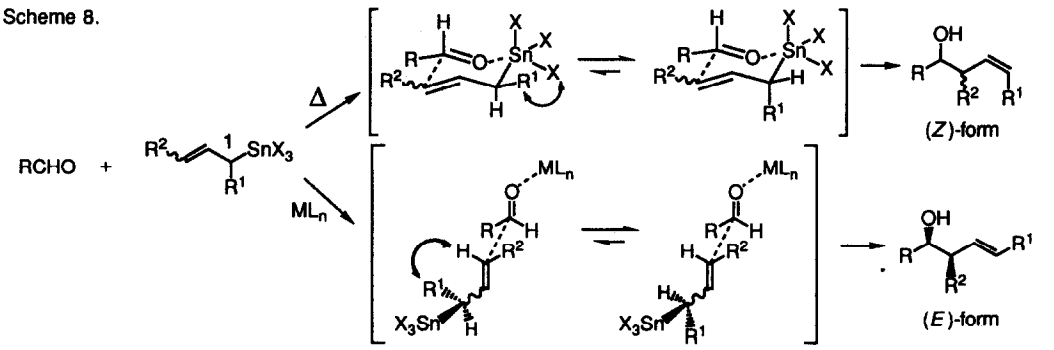
Scheme 7.



Alteration of the transition state, from a cyclic to an acyclic one, by Lewis acids was also reflected in the resultant double bond geometry of the product when 1-substituted allyltins were employed. In the simple

thermal reaction, the (*Z*)-olefin was produced via S_E' allylic rearrangement.[33,58,59] This (*Z*)-preference is thought to be due to the steric congestion between the substituent at C-1 of the allyl moiety and the tin ligand in the transition state (i.e. the substituent at C-1 preferred the axial to the equatorial orientation) (Scheme 8). In

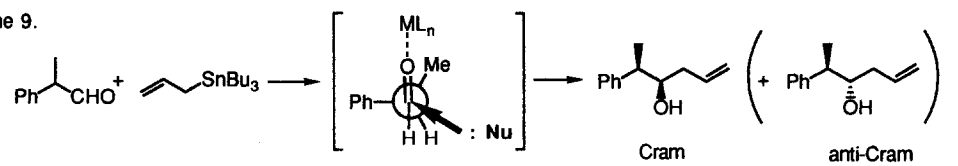
Scheme 8.

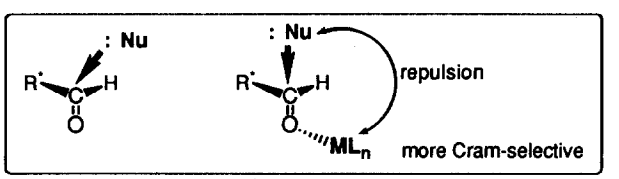


most Lewis acid-promoted reactions, by contrast, the double bond geometry of the resultant product was *E*.[33,39,41,45] This can be caused by avoidance[59a] of the allylic strain produced by the substituent at C-1 of allyltins in the acyclic transition state.[60]

One more example concerning a critical role of simply coordinating a Lewis acid was the induction of Cram selectivity.[27,61] 2-Phenylpropanal was allowed to react with allyltins in the presence of a Lewis acid ($AlCl_3$, $BF_3{\cdot}OEt_2$) (Scheme 9). Compared with the reaction via the cyclic transition state under high pressure,[27] the Cram selectivity (*syn*-selectivity) was much increased. This was explained as follows: the Lewis acid turned the trajectory of the incoming allyltin so as to be closer to the chiral center, probably owing to steric repulsion between the Lewis acid and the allyltin.[2c,62]

Scheme 9.

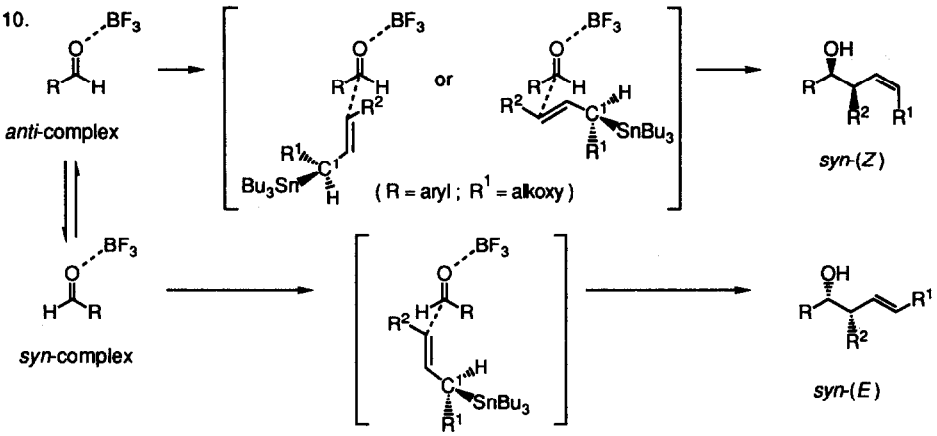




It is worthwhile to mention the reactions of optically active allylic tins, (*E*)-1-alkoxy-3-alkyl-[37,38,63] and (*Z*)-1-alkyl-3-alkoxyallyltins.[64] They are important for mechanistic investigation as well as for synthesis. In both allyltins, the tin atom is attached to the chiral center at C-1. The crotyl-type diastereoselectivity was *syn* as usual. Moreover, the absolute configuration and the double bond geometry of the product confirmed the strict *anti*-S_E' reaction path in the Lewis acid-promoted acyclic system. Although the product double bond geometry was again preferentially *E* in most cases, *Z*-preference was also observed in certain cases of 1-alkoxyallyltins.[63] This was rationalized by an inside alkoxy effect[65] and *syn*/*anti* equilibration of aldehyde-BF_3 complexes. As mentioned above, aromatic aldehydes prefer *anti*-complexation with BF_3,[18] therefore the allylic tin approachs in synclinal and inside alkoxy conformation to avoid the BF_3-substituent at C-3. This results in a (*Z*)-*syn* product. In cases where aliphatic aldehydes are concerned, because of the small energy

difference between the *syn*- and *anti*-complexes,[18] the reaction could occur from the *syn*-complex so that the allylic tin might approach in the antiperiplanar and outside alkoxy conformation. Therefore, the product is the (*E*)-*syn* alcohol, but its absolute configuration is opposite to that of the (*Z*)-*syn* product (Scheme 10). Indeed,

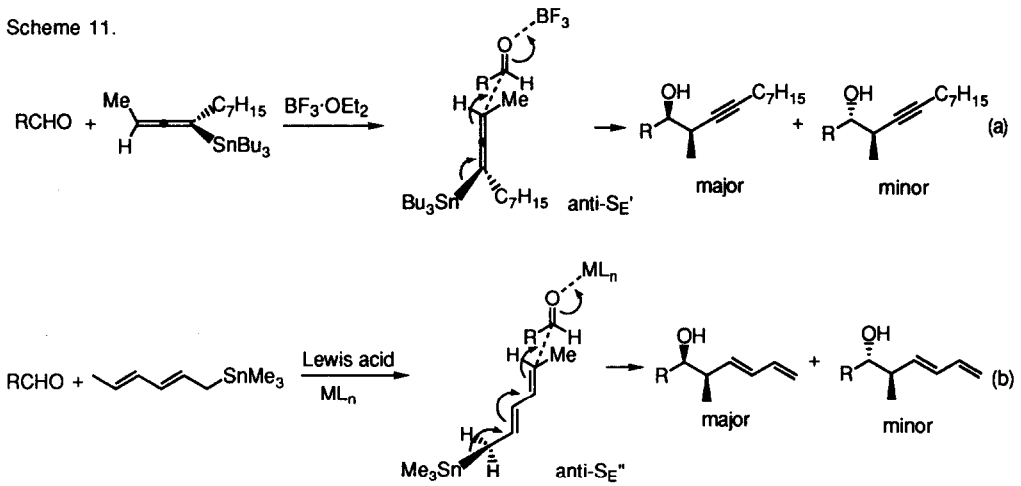
Scheme 10.



the direction of Lewis acid coordination could control the absolute configuration of the product but further investigation should be made for detailed interpretation.

Lewis acid activation also promotes the reactions of allenyltins[66,67] and 2,4-pentadienyltins.[36,68,69] These are attacked by an aldehyde at their terminal 3- and 5-positions via *anti*-S_E'[70] and *anti*-S_E''[71] processes, respectively (Scheme 11). The crotyltin-type diastereoselectivity was also *syn* in both cases.[66,68]

Scheme 11.



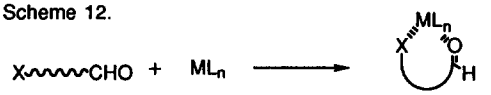
BF_3·OEt_2 has been most conveniently and most frequently used as a simple coordinating Lewis acid activator. Other Lewis acids including Mg, Al, Ti, Zn, and Sn halides (or salts) have also been used, but, as discussed later, it should be kept in mind that interaction between these halides and allylic tins becomes an important factor.

2.2. *Chelation Control of Stereochemistry*

When a carbonyl compound has another coordinating functionality X (Scheme 12; e.g. alkoxy group)

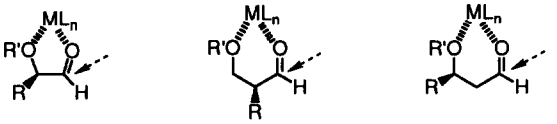
besides the carbonyl, certain Lewis acids can form a chelated complex. In the reaction of such a complex, Lewis acids play two roles: one is as an activator for the carbonyl group as discussed above, and the other, discussed here, is conformational lock of the substrate. The latter role produces stereoselective allylation of the acyclic system by allylic tins. For this purpose, effective chelation is essential and the following three factors are dominant: (i) at least two acceptor sites are required in the Lewis acid for chelation with a substrate, therefore choice of Lewis acids comes important. For non-chelating substrates, the choice is trivial because interaction between a Lewis acid and an allyltin is negligible. (ii) Strength of the coordination bond with the second donating functionality (e.g. alkoxy group). Electronic effects and steric environment affect this factor. (iii) In addition, solvents also affect the chelation according to their donating character.

Scheme 12.

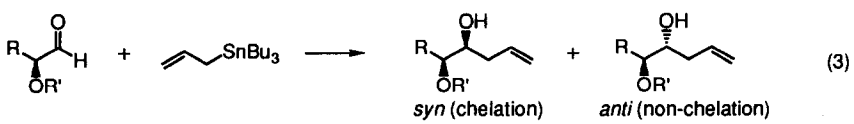


For the chelating role of Lewis acids, $TiCl_4$, $SnCl_4$, $MgBr_2$, and $ZnCl_2$ are those most utilized as expected for factor (i). As a counterpart of the chelate, α- and β-alkoxyaldehydes are most commonly used to form five- and six-membered cyclic complexes, respectively. Because of their thermodynamically stable ring structure, high stereoselectivity is expected. The following three types of stereocontrol are representative (Fig.5): (a) 1,2-asymmetric induction from α-alkoxyaldehydes; (b) 1,2-asymmetric induction from β-alkoxy-α-alkylaldehydes; (c) 1,3-asymmetric induction from β-alkoxyaldehydes. In each type of stereocontrol, an alkyl substituent R on the chelate ring will restrict the direction of the nucleophilic attack, towards the front or the back side of the carbonyl plane. Thus, chelation-controlled stereoselectivity can be realized.

Fig. 5.



In type (a), *syn*-homoallylalcohols were obtained with very high selectivity as reported by Keck's group.[72] The most efficient Lewis acids were $MgBr_2$ and $TiCl_4$, and the alkoxy group should be one which coordinates strongly to the Lewis acid, such as benzyloxy group.[73,74] In contrast, the *t*-butyldimethylsiloxy (TBSO) group showed decreased selectivity even with the use of a chelating Lewis acid, because of its low coordinating ability. This was rationalized in two ways. TBS is a sterically large group, and the silicon atom could withdraw the lone pair of electrons on the oxygen atom by pπ-dπ interaction. This is an example of factor (ii) above.



(3)

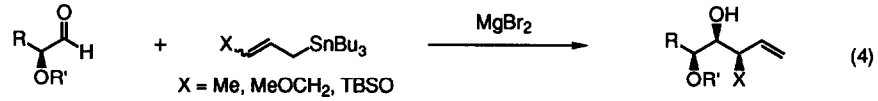
R' = $PhCH_2$, $PhCH_2OCH_2$, $MeOCH_2$, *t*-$BuMe_2Si$ (TBS)

Regarding the choice of solvents (factor iii), non-coordinative CH_2Cl_2 gave the best results.[72] Coordinative ethereal solvents, especially tetrahydrofuran (THF), exhibited low chelation *syn*-selectivity or the reverse *anti*-selectivity (non-chelation, Cram selectivity) even with the use of $MgBr_2$ and a benzyloxy aldehyde. Thus, the ethereal oxygen coordinated with the Lewis acid to neutralise its acceptor site.

When the substrate had two or more coordinating alkoxy groups (e.g. dialdose derivatives),[75] probably

owing to several possible chelation modes, chelative Lewis acids (e.g. $TiCl_4$, $ZnCl_2$) did not undergo highly selective reactions of type (a). Therefore, to achieve high chelation-controlled *syn*-selectivity, TBS protection of the selected OH group (unfavorable to type (a) chelation) was performed.[76,77] Recently, utilization of $LiClO_4$-Et_2O for selective type (a) chelation was reported in the reaction of dialdose derivatives.[78] α-Aminoaldehydes also showed high *syn*-selectivity[79,80] even in the presence of alkoxy groups.[79] This is due to the formation of a stronger complex with the amino group rather than with the alkoxy group.

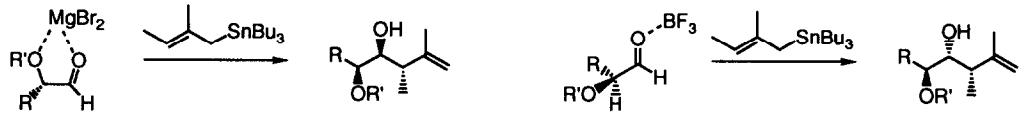
Crotyltins have been used in the chelation controlled reaction.[81] Both chelation controlled *syn*-selectivity and acyclic transition state-induced *syn*-selectivity (*erythro*-selectivity) were realized by the use of coordinative $MgBr_2$. Though $TiCl_4$ established high chelation control, *erythro*-selectivity decreased. This indicates the possibility of transmetalation (discussed later). Other reports about type (a) selectivity by crotyltin[82] and related 3-alkoxyallyltins[83,84] should give similar high *syn*, *syn*-selectivity with $MgBr_2$.



(4)

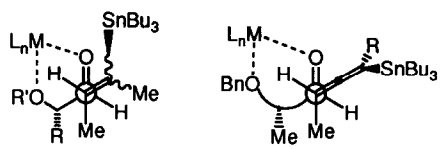
One thing should be noted with this type of the crotyltin reaction. In simple aldehyde activation, the Lewis acid coordinates the carbonyl from the *anti*-direction, whereas in the chelative activation, the coordination is inevitably from the *syn*-direction. This controls the stereochemical outcome. 2-Methylcrotyltin gave an *anti*-(*threo*-)selective alcohol in reaction with a 2-benzyloxyaldehyde and $MgBr_2$, opposite to crotyltin's *syn*-(*erythro*-)selectivity,[82] though chelation controlled *syn*-selectivity remained. *anti*-Coordinating BF_3 showed the usual *syn*-(*erythro*-)selectivity even in the reaction of 2-methylcrotyltin (but non-chelative selectivity) (Scheme 13). Similar reversibility of the stereoselectivity by the applied Lewis acid ($MgBr_2$ or BF_3) was also observed in the reaction of optically active allenyltins.[67,70]

Scheme 13.

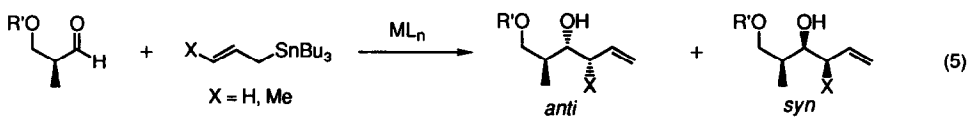


In both instances, the unusual *anti*-(*threo*-)selectivity of crotyl-type tin compounds was accounted for by the synclinal acyclic transition state, which might be induced by the reduced steric congestion between the Lewis acid and the tin reagent in the *syn*-coordinated chelate (Fig. 6).[67,70,82] In the case of both optically active aldehydes and allenyltins, moreover, the combination of the enantiomers was also a stereodefining factor.[67]

Fig. 6.



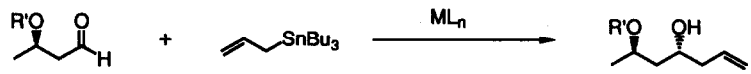
In type (b) with 3-alkoxy-2-methylpropanals, chelative Lewis acids ($TiCl_4$, $SnCl_4$, MgX_2) promoted highly chelation-selective reaction to give *anti*-alcohols.[84,85] The importance of Lewis acid coordination to the



(5)

alkoxy group was demonstrated by the low selectivity in the reaction of siloxy aldehydes.[85] Crotyl-[85,86] and 3-alkoxyallyltins[84] underwent *syn*-(*erythro*-)selective reaction with both these aldehydes and simple aldehydes. Allenyltins were also applied to the type (b) reaction to show high chelation selectivity with $MgBr_2$.[66,67]

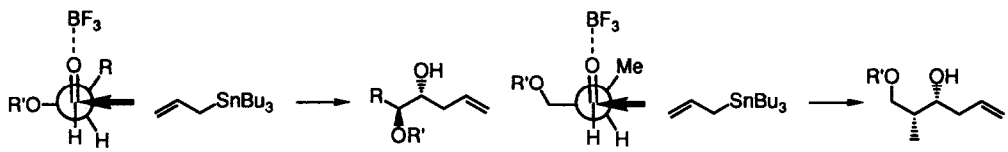
Chelative Lewis acids were again effective for the type (c) reaction. The effects of the Lewis acid, alkoxy group, and aldehyde skeletons on product selectivity were investigated[87] and 1,3-*anti* diol derivatives were obtained with generally high selectivity, especially by the use of $TiCl_4$.[88] In some cases, $MgBr_2$[84,89] and $SnCl_4$[57,90] gave good results. Here again, crotyltin-type *syn*-selectivity was observed.[57,84,89,90]



(6)

In contrast to chelative Lewis acids, non-chelative BF_3·OEt_2, which has only one acceptor site, induced the opposite stereoselectivity; especially in the reaction of types (a)[67,70,72,75,81-83] and (b)[66,67,85]. In both cases, the selectivity was simply explained by the Felkin model of coordinated aldehydes. From the steric and electronic factor (ii), the combination of a TBSO group and BF_3 allowed rather high non-chelative Cram (or Felkin) selectivity: *anti*-selectivity in type (a),[72,82] where the alkoxy group worked as the large group, and *syn*-selectivity in type (b),[85] where the alkoxymethyl (or alkoxyalkyl) group acts as the large group. The effect of the TBS group was interpreted in terms of its steric bulk and electron-withdrawing character as mentioned above and, also, by the lowered $\sigma^*_{C\text{-}O}$ orbital energy due to TBS electron-withdrawing, which stabilized the Felkin model conformation still more (Scheme 14).[72]

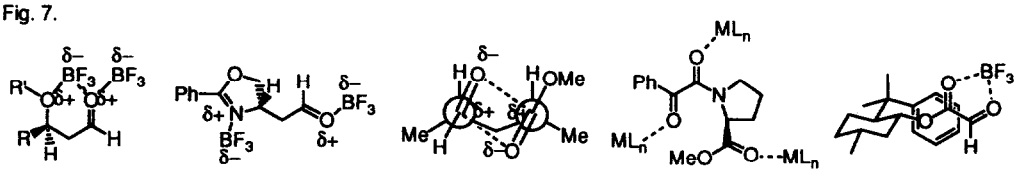
Scheme 14.



Type (a) R' = TBS Type (b) R' = TBS

In spite of the non-chelating character of BF_3, some reports have argued that BF_3 apparently promoted a chelation controlled reaction. In the type (c) reaction, it was posturated that BF_3 exhibited an even higher chelation selectivity than chelative $SnCl_4$.[57] The selectivity was attributed to the electrostatic interaction between the negatively charged coordinating BF_3 and the positively charged carbonyl oxygen (Fig.7a).[91] Parallel results[87] were reported that even in the presence of a TBSO group, BF_3 showed higher *anti*-selectivity, apparently chelating more selective than $TiCl_4$, $MgBr_2$, and $SnCl_4$. Similar selectivity was also published in the reaction of an oxazoline aldehyde.[92] The authors attributed the *anti*-selectivity to the dipole repulsion between the coordinated carbonyl and the also coordinated oxazoline nitrogen (Fig.7b).

Fig. 7.



(a) Electrostatic interaction (b) Dipole repulsion (c) Dipole interaction (d) Saturated coordination (e) Steric block

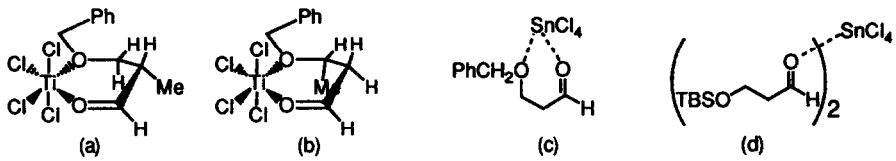
Another instance of apparent BF_3-chelation was given in the reaction of glutaraldehydic ester.[93] It was reported that glutaraldehydic ester alone could take a rigid cyclic conformation due to intramolecular dipole interaction between aldehyde and ester moieties (Fig.7c).[94] It is improbable to assume chelation of BF_3

because it has only one acceptor site.

An additional instance of Lewis acid coordination to an auxiliary determining stereoselectivity was the reported allylation of optically active α-keto amides.[95] The high stereoselectivity was attributed to saturated coordination of the Lewis acid (Fig.7d), which reduced the number of possible conformations of the complex. Inferred from higher selectivity by chelative Lewis acids than by non-chelative ones, chelation may play an important role to fix the conformation of the complex. The bulky phenylmenthyl group was also employed as a chiral auxiliary, which blocked the *re*-face of the chelated glyoxylate (Fig.7e).[27]

Spectroscopic evidence the Lewis acid chelation was given by Keck group's NMR studies[96-98] of the reaction with β-alkoxyaldehydes. It was revealed that β-benzyloxyaldehydes and $TiCl_4$ formed six-membered chelates, and that the α-methyl substituent as seen in the type (b) reaction occupied the pseudoequatorial position (Fig.8a) while β-methyl substituent, as seen in the type (c) reaction, because pseudoaxial to avoid methyl-benzyl repulsion (Fig.8b).[96] Chelation by $SnCl_4$ and $MgBr_2$ (Fig.8c) was also investigated by ^1H, ^{13}C, and ^{119}Sn NMR.[24,97,98] That the TBSO group hindered chelation and favored 2:1-complex formation (Fig.8d) was also shown. These observations explained the selectivities in types (b) and (c) very well.

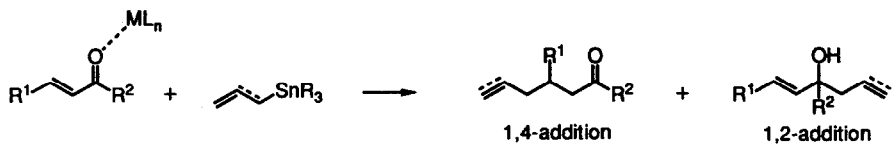
Fig. 8.



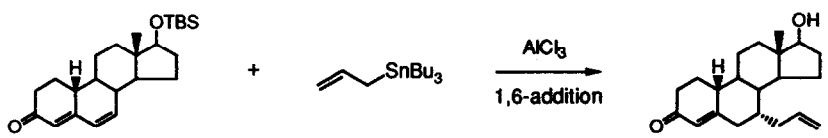
2.3. *Activation of Michael Acceptors Including Quinonoid Compounds*

Lewis acids can also activate Michael acceptors as substrates for the allylstannation reaction. With α,β-unsaturated ketones, the nucleophilic path led to 1,4-addition by the coordination of the Lewis acid (BF_3, $TiCl_4$, $AlCl_3$, etc.),[10,68,99-101] and to 1,2-addition with α,β-unsaturated aldehydes (Scheme 15).[68] The reaction of allenyltins was reported to proceed in 1,4-conjugate fashion most successfully with $TiCl_4$.[102] ZnI_2 in contrast gave 1,2-adducts. The difference in the activation mechanism is still unclear. Indeed, it is difficult to predict correctly which Lewis acid will promote the reaction most effectively. The outcome also appears to depends upon the combination of the substrate and the tin compounds used. In the case of αβ,γδ-unsaturated ketones, even 1,6-conjugate addition was observed (Scheme 16).[103,104]

Scheme 15.



Scheme 16.

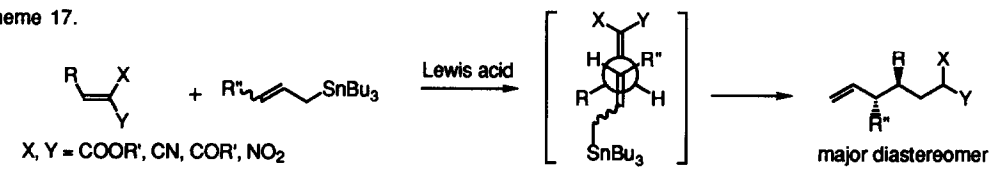


α,β-Unsaturated nitriles,[105] esters,[106] and nitro compounds[100,107] have also been used as Michael acceptors in the Lewis acid-promoted conjugate allylstannation reaction. Here again, stereoselectivites (*erythro*/*threo* in crotyltin reaction and Cram/anti-Cram of chiral Michael acceptors) were reported parallel to those reported in the reactions of aldehydes (Schemes 17 and 18).[100] One interesting investigation on the role of Lewis acids was the reaction of 1,1-dicyanoethylene derivatives, where the Lewis acid ($TiCl_4$) activated the

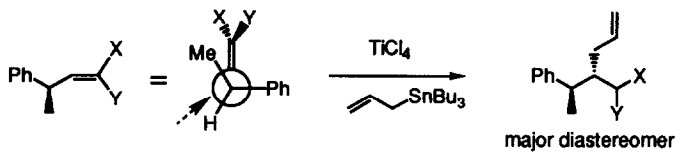
ionic reaction path.[105] The single electron transfer (SET) path, which resulted in opposite stereoselection, did not take place in this reaction system.[105]

Among α,β-unsaturated carbonyl compounds, benzopyranones and α,β-unsaturated acyliron complexes exhibited particular reactivities (Scheme 19). Benzopyranones[108,109] were activated by silyl triflate to

Scheme 17.

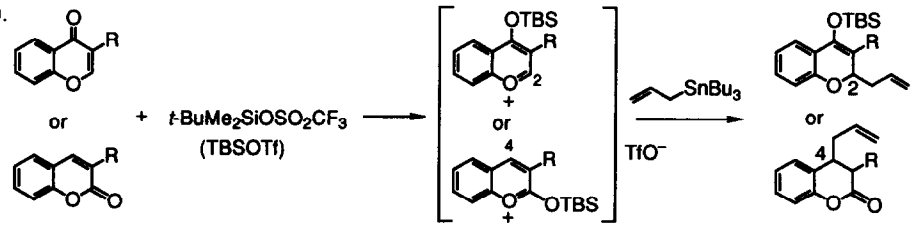


Scheme 18.



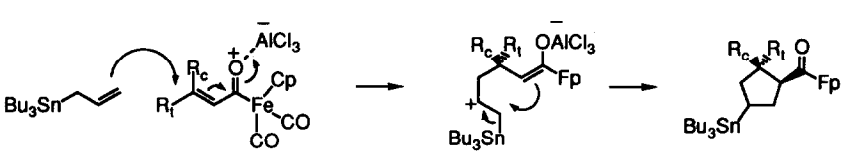
form pyrylium salts, which reacted with allyltins at C-2 or C-4 via the S_E2' path to give allyldihydropyranone derivatives. Though the products were identical with Michael adducts, the Lewis acid (silyl triflate) induced the modified reaction path.

Scheme 19.



In the reaction with acryloyliron complexes,[110-114] the initial role of the Lewis acid ($AlCl_3$) was coordinative activation of the enone portion, which was followed by Michael attack of the allyltins. However, the fate of the reaction was different from that of usual Michael acceptors. Instead of elimination of stannyl cation, which would yield normal Michael adducts, the intermediate enolate reacted by intramolecular nucleophilic attack at the cation center accompanied by stannyl 1,2-migration. As the result, a stannylated cyclopentane ring was constructed (Scheme 20). The strong intramolecular nucleophilicity of the enolate was explained by the strong electron-donating character of the iron complex.[110,113,114] From stereochemical studies,[111,113,114] the cyclization process was very fast or concerted, judged by the high stereospecificity. It was suggested that $AlCl_3$ also worked as a conformational lock for the complex (s-*cis* conformation).[113,114]

Scheme 20.

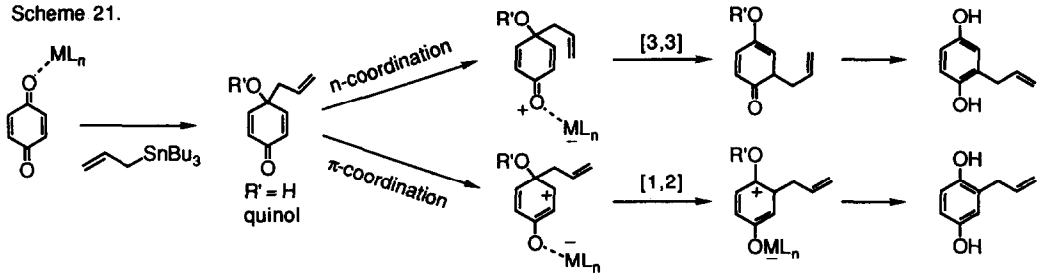


Another interesting kind of substrate among enones are the quinones, which provided the first report on Lewis acid-promoted allylstannation.[7] Quinones are highly electrophilic and introduction of an allyl group nucleophilically by reaction of quinones with anionic allylic reagents does not proceed with high efficiency. The covalent but still significantly polarized C-Sn bond in allylic tins are generally of little used in this respect.

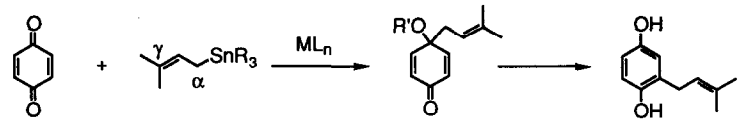
Lewis acid-activation is essential for clean and practical reaction except for some very reactive quinones (e.g. *o*-quinones).[115]

The principal role of Lewis acids (mostly $BF_3{\cdot}OEt_2$) is, of course, coordinative activation of the carbonyl group of the quinone. As depicted by Naruta (Scheme 21),[116] in the reaction of *p*-quinones (*p*-benzoquinones and 1,4-naphthoquinones), the Lewis acid initially promotes 1,2-addition of allylic tins to the carbonyl to give allyl quinols; migration of the introduced allyl moiety onto the aromatic ring (quinol–hydroquinone rearrangement) then occurs if possible. The amount of the Lewis acid as well as the structure of the allylic moiety affects the modes of the initial allylstannation (α- or γ-position of the allyltin) and the successive migration ([1,2] or [3,3], or [1,3] in some cases).[116,117] It was suggested[116,118] that a small amount of Lewis acid underwent energetically favored n-protonation (coordination to n-electrons), leading to thermal [3,3] migration, whereas a large amount increased the contribution of π-protonation (coordination to π-electrons), leading to cationic [1,2] migration. When the γ-terminus of the allyltin was sterically hindered, addition at the α-position (S_E-type reaction) and [1,2] or [1,3] migration were preferred (Scheme 22). Consequently, the allylic double bond geometry was retained in these cases.[117,119-121]

Scheme 21.

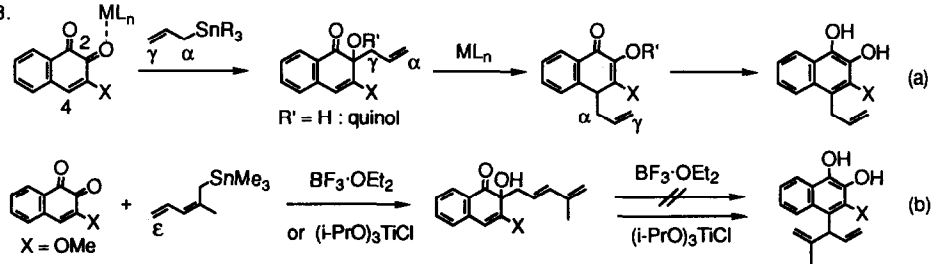


Scheme 22.



A similar feature of allylstannation of 1,2-naphthoquinones was shown by Takuwa group: 1,2-addition to the carbonyl at C-2 and subsequent allylic migration to C-4 (Scheme 23a).[122,123] Indeed, in the cases of both *p*- and *o*-quinones, quinol intermediates were isolated and the allyl migration took place independently.[116,123] As a special instance, the reaction of 1,2-naphthoquinones and pentadienyltin[115] ceased at the 1,2-addition step when $BF_3{\cdot}OEt_2$ was used. Use of $(i\text{-PrO})_3TiCl$ as Lewis acid led to the [3,3] migration and gave a branched dienyl chain at C-4 (Scheme 23b). This observation confirmed the dual role of the Lewis acids and showed that the allylic migration preferred the thermally allowed [3,3] pathway.[115]

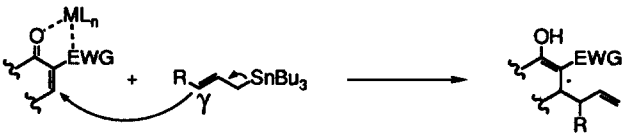
Scheme 23.



When quinones were activated by an electron-withdrawing substituent (e.g. 2-alkanoyl-1,4-

quinones,[124,125] 3-nitro- and 3-alkanoyl-1,2-naphthoquinones[115,123]), Lewis acids then induced direct 1,4-addition (Michael addition). This was characterized by regioselective addition at the terminal of the allylic tin (γ-position to the tin atom for allyltins and ε-position for pentadienyltins) *via* the S_E' allylic rearrangement (Scheme 24). When the 1,2-addition/migration path featured in the reaction, the regiochemistry of the introduced allyl moiety became diverse and depended upon the structures of the quinones and the allylic moieties.[116,117] In the particular case of pentadienyltins, bidentate Lewis acids (e.g. $(i\text{-PrO})_3TiCl$, $SnCl_4$) gave better yields than $BF_3{\cdot}OEt_2$.[126,127] This was presumably because chelation between quinone carbonyl and alkanoyl carbonyl resulted in more selective activation at the C=C double bond. Monodentate Lewis acids such as BF_3 and $AlCl_3$ were suitable for the introduction of a conjugated diene into simple quinones.[68,128]

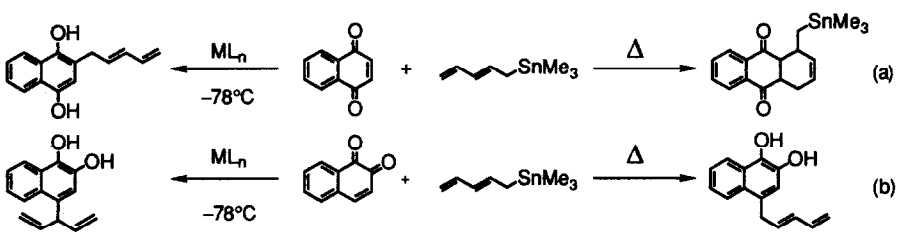
Scheme 24.



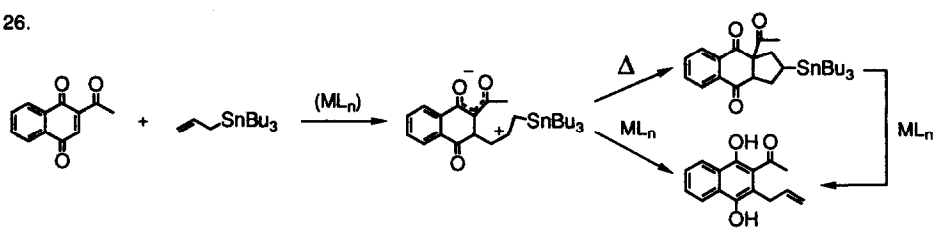
It is valuable to compare the reactions of quinones and allyltins with and without Lewis acids to understand the role of the Lewis acids. Labile 1,4- and 1,2-quinones can react with certain allyl tins even in the absence of Lewis acids. The reactions of pentadienyltins are indicative. With 1,4-quinones (Scheme 25a), they undergo very efficientl Diels-Alder cyclization as an electron-rich diene.[129] In contrast, under Lewis acid-promoted conditions, smooth nucleophilic pentadienylation takes place. This difference indicates that Lewis acids polarize the quinones to promote the ionic electrophilic reaction.

In the case of 1,2-naphthoquinones (Scheme 25b),[115] no Diels-Alder reaction proceeded with pentadienyltins; quantitative Michael-type pentadienylstannation was observed even in the absence of Lewis acids. This reflects that 1,2-quinones are themselves more polarized than 1,4-quinones. Another interpretation was that the reaction was initiated by SET from the tin compound to the 1,2-quinone, which is more reducible than the corresponding 1,4-quinone.[115] The Lewis acids induced polarization of the quinone, which underwent S_E'' attack on pentadienyltin as noted above.

Scheme 25.



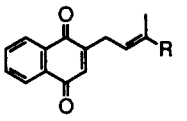
Scheme 26.



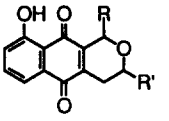
Combination of allyltin and 2-alkanoyl-1,4-quinone also resulted in thermal reaction without Lewis acids (Scheme 26).[130] This gave various products with low selectivity, including stannylated cyclopentane, which indicated that one role of the Lewis acid was to eliminate the stannyl group from the intermediate as a cation.

These Lewis acid-promoted reactions of quinones have been successfully well applied to the synthesis of naturally occurring quinones, prenylquinones, [119-121,131] pyranonaphthoquinones,[125,132] anthracyclinones,[126,127,133-135] and so on (Fig. 9).[127,136] Some of these can be obtained on a preparative scale in high yield.[137] For high synthetic efficiency, Lewis acids should be selected not only from the viewpoint of the activation of quinones but also from the selectivity of the reaction and avoidance of decomposition of delicate substrates and reagents (e.g. labile and optically active substituents).[127,135]

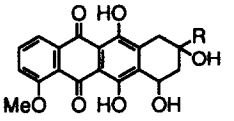
Fig. 9.



Prenylquinone

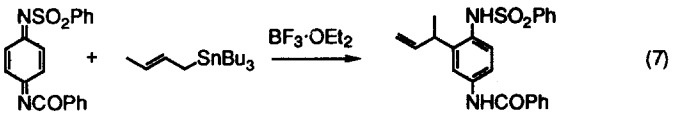


Pyranonaphthoquinone



Anthracyclinone

p-Quinone diimides are also activated by $BF_3{\cdot}OEt_2$ as Michael acceptors toward allylic tins.[138] The Lewis acid coordinated to the more basic nitrogen (=NCOPh > $=NSO_2Ph$) and this led to regioselective allylation. S_E' Type allylation reaction directly onto the quinonoid nucleus was reported.

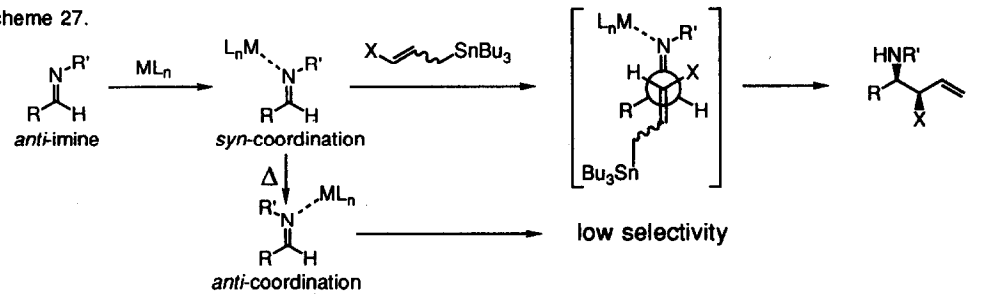


(7)

2.4. *Activation of Nitrogen-Containing Electrophiles*

As nitrogen analogues of aldehydes, imines also undergo Lewis acid-promoted allylstannation. Three reports appeared in succession in 1985.[75,139,140] $BF_3{\cdot}OEt_2$ and $TiCl_4$ were used as activators, because neither high temperature nor high pressure promoted the reaction.[140] Reaction with crotyltin and crotyl-type (3-substituted allyl) tins proceeded in a stereoselective fashion[140, 141] but with less *syn*-selectively than the reaction of aldehydes. Therefore the antiperiplanar transition state proposed for the reaction of aldehydes[26] was again probable (Scheme 27).[140] Cram-selectivity was also similar to that observed for aldehydes.[142] High *syn*-selectivity was reported by the use of $TiCl_4$. In this reaction, however, the actual reagent was presumed to be an allyltitanium formed by transmetalation (discussed in Section 3.1). Moderate selectivity was obtained by BF_3-promotion.

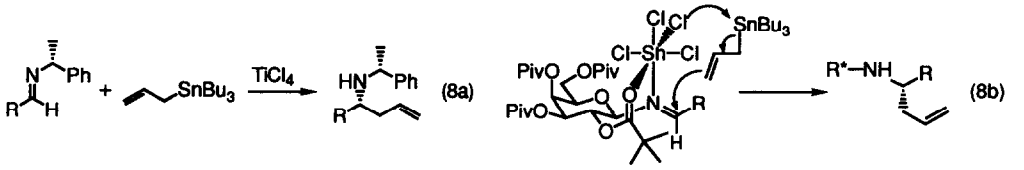
Scheme 27.



One critical difference between the structure of the aldehyde and an imine is the presence of a substituent on the hetero atom (nitrogen of imine). The most configurationally stable imine is the *anti*-isomer, so complexation by Lewis acids is kinetically directed towards the *syn*-configuration at low temperature. The *syn*-complex promotes high *syn*-selectivity with crotyltin as noted by Keck.[139] The *anti*-complex, which is thermodynamically more stable at higher temperature (accompanied by isomerization to *syn*-imine), seems to induce lower selectivity. This indicates that the role of the Lewis acid is not merely simple activation of the

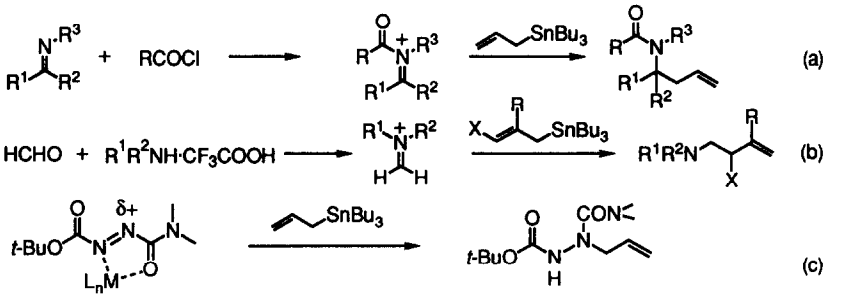
imine but also control of stereoselectivity by steric (or stereoelectronic) influence.

When the *N*-substituent on an imine had a chiral center (e.g. derivatives from α-phenethylamine and glycosylamine) then asymmetric induction was realized.[142,143] Stereoselective reaction induced by a chiral auxiliary was not possible with aldehydes. For this purpose, $TiCl_4$ was more effective than $BF_3{\cdot}OEt_2$, though the $TiCl_4$-promoted reaction proceeded via transmetalation (eq. 8a; see section 3.1).[142] Glycosylimine participated in the $SnCl_4$-mediated reaction: $SnCl_4$ could chelate the substrate so as to fix the conformation (steric block; eq.8b).[143]



Acid chlorides worked both as an activator like Lewis acids and as a reagent to form amides in the allylation of imines and nitrogen aromatics.[144-148] They formed reactive iminium salts which were the actual electrophiles (Scheme 28). This method has been applied in alkaloid synthesis.[146,148] As another example of the reactions of iminium salts, allylstannation of formaldehyde in the presence of an ammonium salt derived from a primary or secondary amine and a protic acid has been reported.[149,150] The ammonium salt can be considered as an activator like Lewis acids. In this reaction, homoallylamines were formed.

Scheme 28.

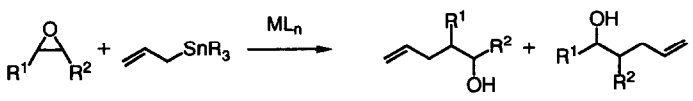


In addition to C=O and C=N electrophiles, N=N electrophiles, azodicarbonyl compounds, have also been utilized for allylation.[151] Lewis acid-chelation promoted regioselective activation of the electrophilic nitrogen center (Scheme 28c).[152]

2.5. *Activation of Substitution Reactions*

In this section we deal with Lewis acid-promoted *substitution* reactions. For such reactions, ethereal substrates, oxiranes and acetals, are the most well-known. Lewis acids coordinate an ethereal oxygen, a Lewis base, so as to polarize the O-C bond (Scheme 29). As the positive charge on the carbon atom develops then allylation by allylic tins proceeds via the S_N pathway.

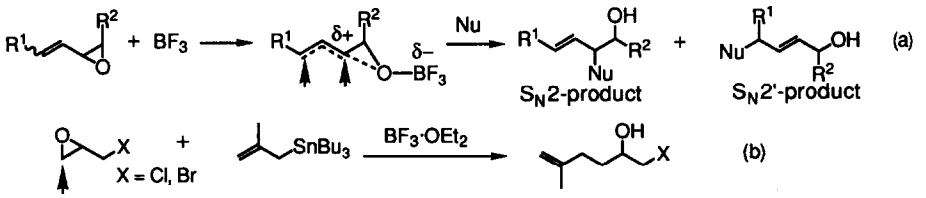
Scheme 29.



Bond strain in oxiranes can be a good driving force for the substitution reaction. Intermolecular allylations of oxiranes are known. Vinyl epoxides[153,154] and epihalohydrins[155] have been used for the efficient reaction. Otherwise, it might be a problem to allylate a particular site of the oxirane ring and to suppress

Lewis acid-promoted isomerization of the oxiranes. For vinyl epoxides (Scheme 30a), the Lewis acid (BF_3-OEt_2 was most efficient) produced a cationic center at the vinyl-substituted carbon of the oxirane due to allylic conjugation, and hence allylation occurred at this site via either the S_N2 pathway[153,154] or the S_N2' pathway[154] depending upon the substituents. Epihalohydrins were also activated regioselectively at the unsubstituted oxirane carbon to afford halohydrins (Scheme 30b).[155]

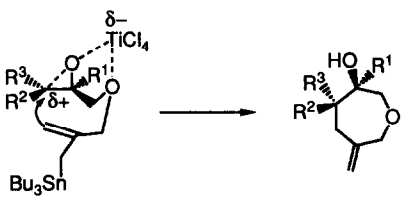
Scheme 30.



When both an oxirane and an allylic tin are present in the same molecule, Lewis acids can activate the oxirane without affecting the tin substituent.[156-160] The choice of Lewis acid for this system depended upon the substrate. $TiCl_4$ was favored in certain instances,[157,158,160] but in another it was disfavored.[159] As for BF_3-OEt_2, $SnCl_4$, Me_3SiOTf and so on, similar preference was encountered.[156-160] In one case, even protic CF_3COOH was of use.[156]

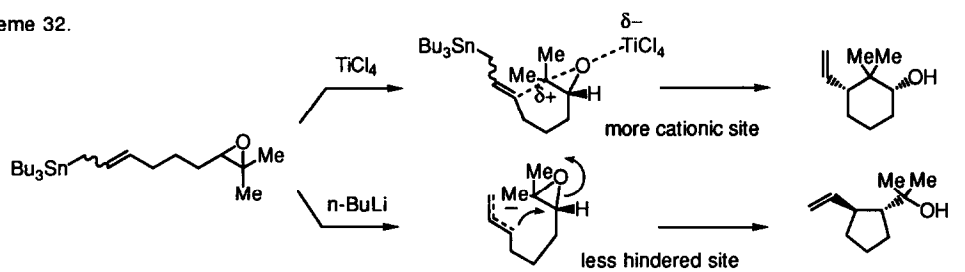
Lewis acid-dependence and effect of substituents on an oxirane ring determine the whole regio- and stereo-selectivity; cation-stabilizing substituents control the substitution reaction.[156-160] Another regio-controlling factor can be seen in chelative activation by bidentate $TiCl_4$ (Scheme 31).[157] Chelation limits the coordinating direction of $TiCl_4$ so that the cation center is generated regioselectively.

Scheme 31.



Lewis acid-promoted reaction (borderline S_N2) has been compared with anionic reaction (typical S_N2),[160] where the steric effect of the substituents (not cation stability) determines the regio-selectivity. This has made the role of Lewis acids clearer (Scheme 32).

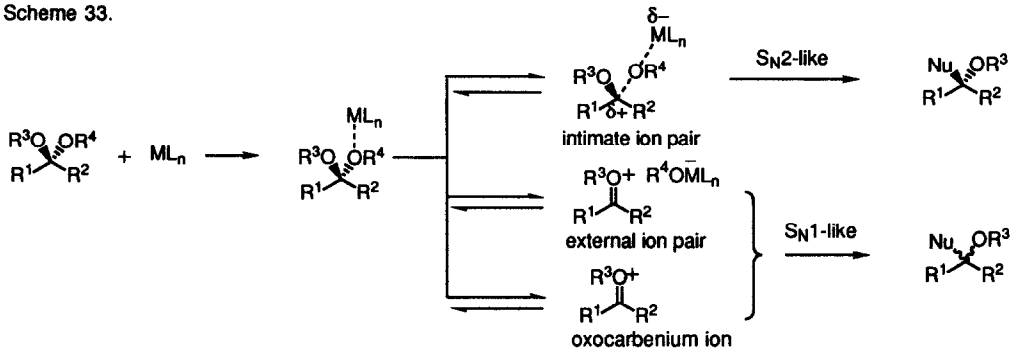
Scheme 32.



Acetals are another group of the substrates subject to the substitution reaction. Two alkoxy groups on the same carbon facilitate positive charge formation on this carbon (Scheme 33). That Lewis acids can activate acetals to allylation by stannanes was known as early as 1979,[10] but versatile application and mechanistic investigation was not carried out until several years later. Much attention has been paid to the stereoselective reaction of chiral acetals (especially cyclic ones) as chiral carbonyl equivalents.

Insight into this reaction has been obtained recently by the Denmark[161-165] and the Yamamoto groups.[166,167] By NMR study of coordinated acetals and the intramolecular reaction of conformationally restricted stannylacetals, it was shown that three factors dominate the stereoselectivity: (i) the structure of the acetal template, (ii) the coordinating strength of the applied Lewis acid, and (iii) the nucleophilicity of the reagent (Scheme 33). NMR study[162,163] revealed that Lewis acids preferentially coordinate to the sterically less hindered oxygen, so that it can be substituted by a nucleophile. The stronger the coordinating Lewis

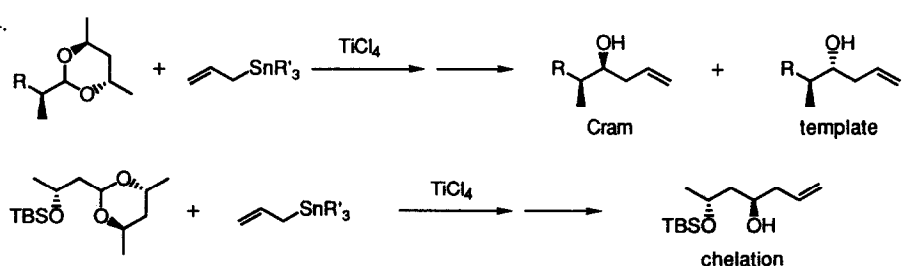
Scheme 33.



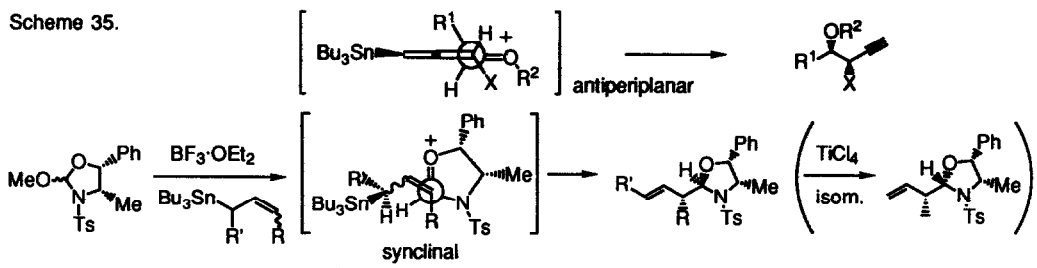
acid (e.g. $TiCl_4$, $SnCl_4$), the more oxocarbenium ion character the reaction center possesses. In other words, the weaker Lewis acids (e.g. $TiCl_4/Ti(OPr\text{-}i)_4$, $BF_3{\cdot}OEt_2$) show more intimate ion pair character. It is interesting that Lewis acidity can be controlled by varying the ratio of $TiCl_4/Ti(OPr\text{-}i)_4$, which has been described as "Ti-blend". In addition, a better nucleophile such as allyl*tributyl*tin could capture the intimate ion pair, whereas a poorer one such as allyl*triphenyl*tin requires the more ionic intermediate.[165,166] Less nucleophilic allylsilanes and allylgermanes behaved similarly.[165,166,168] The combination of the Lewis acidity and the nucleophilicity determines which transition state, S_N1-like oxocarbenium ion or S_N2-like intimate ion pair, operates.

In the latter case (the combination of weaker Lewis acid and/or powerful nucleophile), nucleophilic allyltins attack from the back-side of the departing alkoxy group. Thus high stereoselectivity (inversion) based upon the acetal template was realized.[164-166] In the former case (the combination of powerful Lewis acid and weaker nucleophile), template control was not expected, but substrate control Cram or chelation-control like that for aldehydes, was dominant (Scheme 34).[166,167] Similarly, this type of control is also seen in crotyltin-type *syn*-(*erythro*-)selectivity *via* acyclic antiperiplanar transition state, particularly in the reaction of substituted allenyltins (Scheme 35).[169] Only low selectivity was observed in such S_N1-like oxocarbenium reactions. Allylation with high stereoselectivity was reported in the reaction of the methoxyoxazolidines derived from norephedrine.[170,171] Developed oxocarbenium ion was attacked by crotyltin and 3-alkoxyallyltin in synclinal geometry to give a single stereoisomer, *trans*-substitution to phenyl and methyl groups. While $BF_3{\cdot}OEt_2$ gave this isomer as the product, it should be noted that $TiCl_4$ induced subsequent isomerization gave the *cis*-product.[170]

Scheme 34.

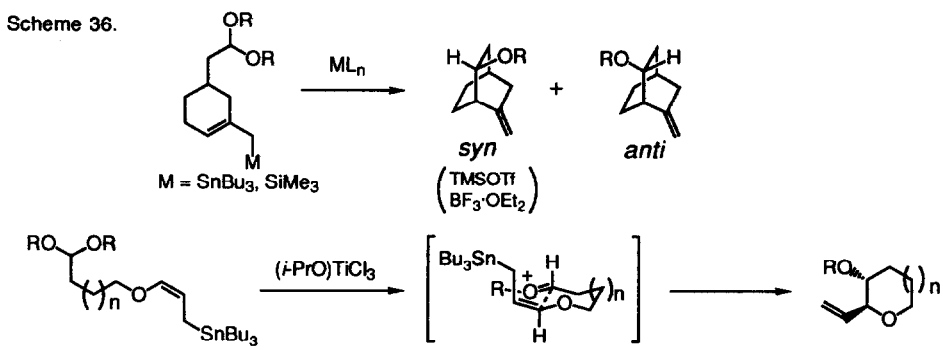


Scheme 35.



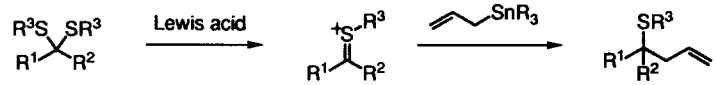
A similar concept was valid for the intramolecular reaction (Scheme 36). Again, for high selectivity, Lewis acids should be weak and monodentate in order to direct the reaction via S_N2-like path.[161,163] When bidentate ligands ($TiCl_4$, $SnCl_4$) chelated both acetal oxygens to form carbenium cation, the selectivity was generally low. Thus, the importance of the timing of bond-breaking and bond-forming for steric control should be stressed. In a case of the intramolecular S_N1 reaction, trans-selectivity was moderately preferred *via* a cyclic and synclinal transition state with use of (*i*-PrO)$TiCl_3$ as the Lewis acid.[172]

Scheme 36.



An additional interesting example of Lewis acid-promoted substitution reaction is that of thioacetals (Scheme 37). For effective activation, suitable Lewis acids should be designed carefully. $(Me_2SSMe)^+BF_4^-$

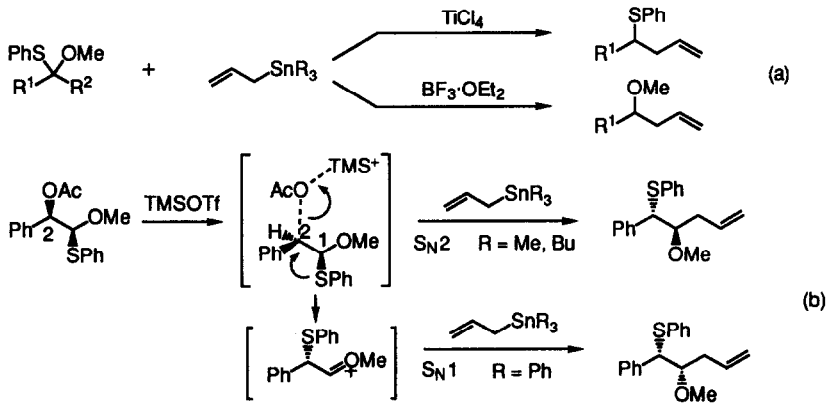
Scheme 37.



(DMTSF)[173] and $GaCl_3$[174] has been reported. The former is known to induce selective activation of the thioacetal moiety in the presence of various other functionalities. The reaction appears to proceed via the corresponding thionium intermediate. For the latter Lewis acid, it was said that its softness was essential for high thiophilicity.

In the reaction of mono-thioacetals,[175] 1-methoxy-1-phenylthioalkanes, chemoselective activation (activation of C-O bond or C-S bond) was determined by the Lewis acid (Scheme 38a). By the use of $TiCl_4$, homoallyl thioether was produced *via* methoxy elimination due to the extremely high oxygen affinity of $TiCl_4$. In contrast, BF_3·OEt_2 induced homoallyl ether formation *via* phenylthio elimination because of the high affinity between Sn and S atoms and the stability of the oxocarbenium ion. When an acetoxy group was substituted at the 2-position of the thioacetal (Scheme 38b), Me_3SiOTf could activate the substrate.[176] But the initial activated site (i.e. coordination site of Me_3Si^+) was not the acetal moiety. Unusually, the silyl cation attacked the acetoxy group. Then, nucleophilic attack occurred at the acetal moiety accompanied by 1,2-migration of the thio group. Here again, stereospecificity and selectivity were dependent on the reaction path,

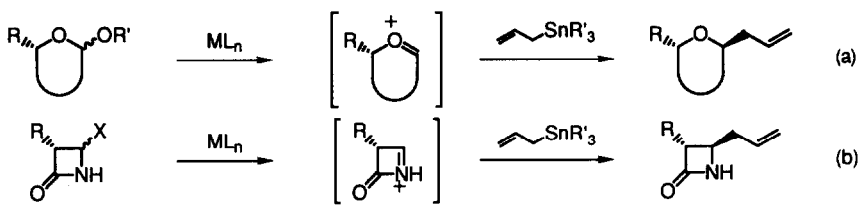
Scheme 38.



S_N1 or S_N2, determined by the Lewis acidity and the nucleophilicity of the reagent.

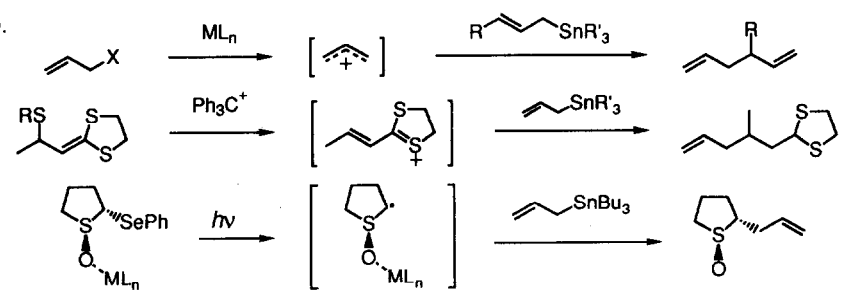
Substitutional allylation of acetals and acetal-like compounds has offered a method for stereoselective synthesis of natural products. Cyclic acetal derivatives such as lactols (Scheme 39a)[177,178] and β-X-β-lactams (Scheme 39b)[179-181] has been widely utilized. $BF_3{\cdot}OEt_2$, and in some case Me_3SiOTf, gave the best results. The reaction seems to proceed via cationic intermediates (oxocarbenium and iminium ions), i.e. S_N1 path, because the substituted products all have the *trans*-configuration from steric requirements regardless of the starting stereochemistry.

Scheme 39.



One more group of substrates employed in the substitution reaction is allyl halides[182-184] and allyl alcohol derivatives.[184,185] Lewis acids coordinate to form a stable allyl cation, which is attacked by nucleophilic allyltins (Scheme 40).[183] This produces biallyl compounds which allyl-rearrange *via* the S_E' path. In a case of substitution of the OH group, a Lewis acid-amine complex was used for the removal of the proton produced. A similar substitution reaction has been reported with diarylmethyl chlorides,[186] where the S_N1 path was confirmed by the fact that Lewis acids had no effect on the reaction rate. As a similar reaction to the above, substitution of allyl sulfides was catalyzed by trityl (triphenylmethyl) cation as a Lewis acid.[187] Azides[187a] and triflates[187b] were also substituted with the aid of Lewis acids. Even in a radical substitution

Scheme 40.



reaction of a selenosulfoxide, Lewis acids played an important role by enhancing the stereoselectivity by coordination to the sulfoxide moiety.[188]

Lewis acids also activate acyl chlorides to give allyl ketones *via* substitution reaction at the sp^2 carbon.[189,190] Most of these reactions are promoted by transition metal catalysts.[1c,4]

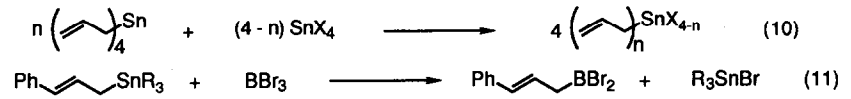
3. ACTIVATION OF ALLYLIC TIN REAGENTS. INTERACTION BETWEEN LEWIS ACIDS AND ALLYLTINS

We now discuss the interaction between Lewis acids and allyltins, to which very little attention has been paid so far. Interaction between Lewis acids and electrophiles has been well demonstrated in the previous section 2. However, one should keep this in mind when considering the allyltin reaction and its synthetic applications. This role of Lewis acids is characteristic for the reaction with tin compounds due to their larger σ–π conjugation compared to that of homologous allylsilanes.

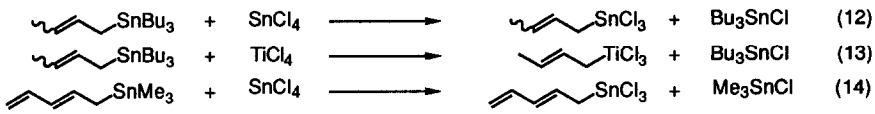
3.1. *Transmetalation Reaction*

In general, "transmetalation" means metal-metal exchange reaction, and the term can be used for the reaction between an allylic tin and a Lewis acid (or a metal salt) as shown by the following equation:

It has also been called a "redistribution reaction" or "metathesis". It was known as early as 1970 for the reaction between tetraallyltin and tin (IV) halides, which gives various allyltin halides according to the stoichiometry of the two reactants.[191] In 1971, in the study of the reaction of trialkylcinnamyltin and BBr_3, selective cinnamyl transfer from the tin to the boron atom was reported, presumably proceeding through a four or six-membered cyclic transition state.[192]



In spite of these early findings, no attention was initially paid to the possibility of transmetalation in the allyltin-Lewis acid reaction system. Reports concerning the transmetalation reaction between allylic tins and Lewis acids appeared in 1984 on the reaction of crotyltin and $SnCl_4$, $TiCl_4$[34,85] and in 1986 on the reaction of pentadienyltin and $SnCl_4$.[193] In both cases, the resultant allylic metals were examined as new reagents showing modified reactivity compared with the parent allylic trialkyltin reagents.



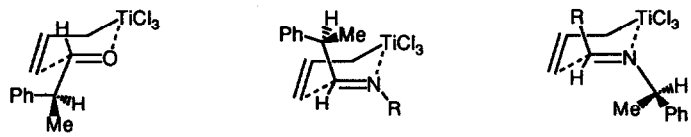
After these reports, several applications appeared utilizing the transmetalation of allylic tins with Lewis acids, especially $TiCl_4$.[33,44,142,194] In these cases, the actual reacting species was not the parent allylic tin reagent but allylic trichlorotitanium, which had not previously been identified spectroscopically. Taking advantage of the strong *E*-preference of the transmetalated crotyltitanium[34] and strong coordinativity of the $TiCl_3$ moiety to polar groups, the transition state of the reaction toward aldehydes was altered to cyclic from acyclic, affording products in *anti*-(*threo*-)selectivity (Scheme 41).[33,34,44,194] Optically active allyltin was also employed in this reaction.[195] In the corresponding intramolecular reaction, the formation of an (*E*)-titanium reagent also contributed to the high stereoselectivity, compared with the reaction by non-transmetalating

Scheme 41.

$EtAlCl_2$.[103] An allylic tin possessing a coordinating functionality exhibited no selectivity *via* transmetalation.[43] When there is stereoisomerism around the resultant double bond, the product has *E*-geometry generated *via* a six-membered cyclic transition state (*cf.* section 2.1).[33,194]

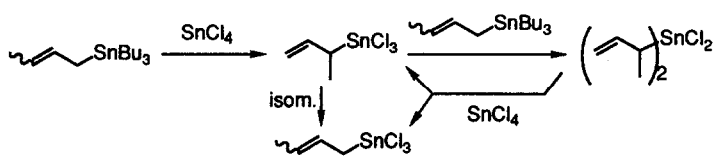
Unless the initial transmetalation was independently carried out by inverse addition, transmetalation appeared to proceed as a side reaction in some cases due to high reactivity even at low temperatures. In particular, the asymmetric induction from a chiral aldehyde was found to show poorer Cram selectivity by the use of $TiCl_4$ than by the use of non-transmetalating $BF_3{\cdot}OEt_2$ or $AlCl_3$.[27,85,196] It was concluded that this involved the formation of allylic titanium *in situ* from $TiCl_4$, followed by reaction with the carbonyl compound *via* a cyclic transition state (Fig. 10, *cf.* Section 2.1). In the reaction with imines, slow formation of a $TiCl_4$-imine complex, especially at low temperature, led to caused preferential transmetalation with resulting reaction of allyltitanium.[142] Higher asymmetric induction from chiral imines was realized than that in the reaction by simple Lewis acid activation of the imines. This contrast in selectivity between aldehydes and imines was probably due to a difference between the conformations of the six-membered cyclic transition complexes.[142]

Fig. 10.



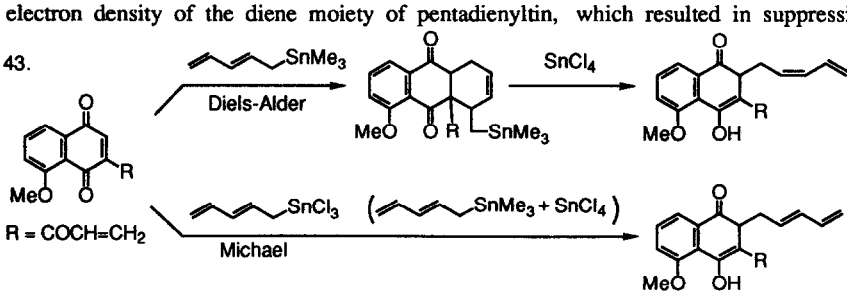
Transmetalation reactions of $SnCl_4$ have been well characterized by means of ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy, in contrast with those with $TiCl_4$.[22-24,197] Only free $SnCl_4$ (not complexed with aldehydes) underwent transmetalation[24] and it was shown how the subsequent addition reaction to aldehydes proceeded.[22-24] In addition the features of the transmetalations of crotyltin (initial formation of trichloro(1-methylallyl)tin and consecutive isomerization to the corresponding (*Z*)- and (*E*)-crotyltins; Scheme 42) and

Scheme 42.



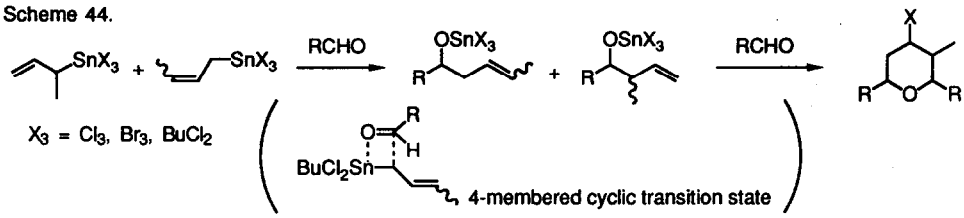
pentadienyltin (isomeric distribution and fluxionality of (*Z*)-trichloropentadienyltin) were reported.[197] For important roles of $SnCl_4$-transmetalation, one can show strong coordination of the $SnCl_3$ moiety, which in one case resulted in high stereoselectivity,[85] as well as the electron-withdrawing effect of the $SnCl_3$ moiety.[198] This decreased the electron density of the diene moiety of pentadienyltin, which resulted in suppression of

Scheme 43.



undesirable Diels-Alder reaction (Scheme 43).[127,193] Tagliavini and co-workers[199] also suggested that allyltrialkyltin and SnX_4 (X = Cl, Br) formed allyltrihalotins, which then reacted with two equivalents of aldehydes to give tetrahydropyran derivatives (Scheme 44). They also commented that the lower Lewis acidity

Scheme 44.

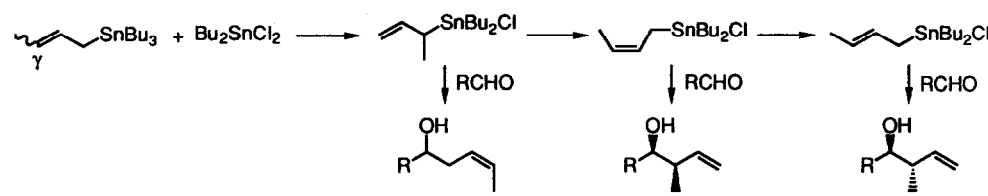


($SnCl_4$ > $SnBr_4$ > $BuSnCl_3$) increased the proportion of the transmetalated (*Z*)-crotyltin and the more stereoselective formation of the tetrahydropyran in the further reaction with the aldehyde.[200] A couple of reactions involving $SnCl_4$-transmetalation were also presented.[158,186]

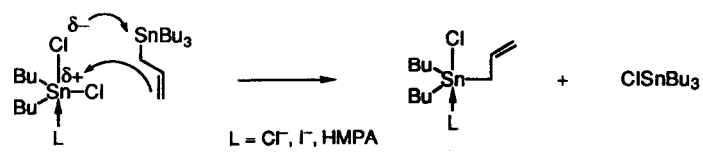
$BuSnCl_3$ and Bu_2SnCl_2 also undergo similar but much slower transmetalation reactions than $SnCl_4$ with allylic tins. They were considered as redistributing reagents rather than Lewis acids. Allyl-[198] and crotyltins[201,202] with $BuSnCl_3$ afforded the corresponding allylic butyldichlorotins, which then added to one equivalent of aldehyde giving the corresponding homoallyl alcohols. A four-membered cyclic transition state was suggested[201] for the formation of the α-adducts. When one more equivalent of aldehyde was present in the reaction system then the tetrahydropyran formed, as above.[200-202]

The reaction between Bu_2SnCl_2 and crotyltin has been extensively investigated.[203] It seems that the transmetalation reaction proceeds substantially *via* the same path as that of $SnCl_4$ in the following three stages: (i) initial formation of dibutylchloro(1-methylallyl)tin through reaction at the terminal γ-position of the crotyltin, (ii) subsequent and preferential isomerization to the corresponding (*Z*)-crotyltin, and (iii) gradual isomerization to the thermodynamically more stable *E*-isomer. These three transmetalated allylic dibutylchlorotins react with an aldehyde to give (*Z*)-linear, *syn*-branched, and *anti*-branched homoallyl alcohols via cyclic transition states (Scheme 45).[48,59] Recently, it was reported that this transmetalation by Bu_2SnCl_2 was accelerated by the addition of Cl^-, I^- or hexamethylphosphoramide (HMPA) as a ligand[204-206] Coordination of the fifth ligand increased both the Lewis acidity of the ligated tin atom[207] and the polarity of the Sn-Cl bond. Thus the electrophilic attack of the tin atom and the nucleophilic attack of the chloride of Bu_2SnCl_2 to the allylic tin were enhanced to complete the transmetalation reaction (Scheme 46).[204] The resultant allyltin used for reaction with acid chlorides,[204] α-haloketones,[205] and aldehydes[206] where Bu_2SnCl_2·L worked as a catalyst for the transmetalation rather than as a Lewis acid for the activation of the substrates. Transmetallation of allyltins by Bu_2SnCl_2 has also been reported.[207a]

Scheme 45.

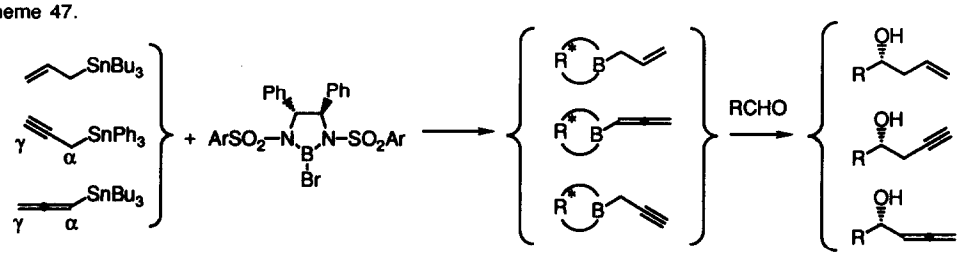


Scheme 46.



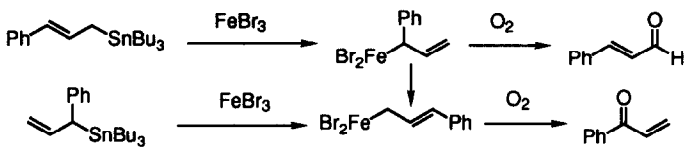
Though BF_3·OEt_2 does not undergo a transmetalation reaction with allylic tins (*cf.* 3.2), BCl_3[186,208] and BBr_3[209] do. It was only recently that the reaction was applied synthetically to sophisticated systems although this reaction has been recognized for a long time.[192] Optically active boron bromides were employed in the transmetalation reaction with allenyl, propargyl,[210] and allyltins.[211] This gave the corresponding optically active organoboranes which could be utilized for efficient asymmetric synthesis (Scheme 47). Here again, the transmetalation reaction was accompanied by allylic rearrangement;[212] allenyltin gave the propargylborane and propargyltin gave the allenylborane. Other examples of the transmetalation by boron chloride were reported.[210] Reactions with aldehydes were compared between BF_3·OEt_2 and BCl_3.[208]

Scheme 47.



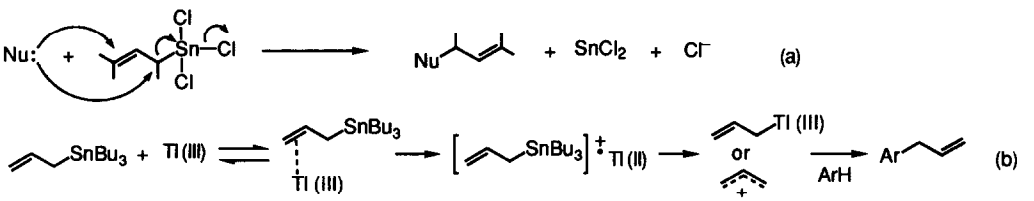
Reactions *via* transmetalation with other Lewis acidic metal halides have been reported. In the $AlCl_3$-*i*-PrOH mediated allylstannation reaction of aldehydes, formation of an allylaluminium was suggested.[213] In $FeBr_3$-mediated autoxidation of cinnamyl- and 1-phenylallyltins,[214] transmetalation to cinnamyl- and 1-phenylallylirons *via* the allyl rearrangement was indicated from the regioselectivity of the oxidation with molecular oxygen (Scheme 48). Transmetalations between benzyltin and $HgCl_2$[215] and between cyclopentadienyltin and $ZrCl_4$·$(SMe_2)_2$ and $HfCl_4$·$(SMe_2)_2$[216] were also reported but not applied to synthetic reactions.

Scheme 48.



Formal $SnCl_4$-mediated *electrophilic* reaction of allylic tins is known.[217,218] The allylic tin was initially transmetalated to the corresponding allylic trichlorotin which then provided an allylic cation equivalent. (Scheme 49a). Similarly, oxidizing metal compounds such as $TiCl_4$,[217] Cu(II) salts,[217,219,220] and Tl(III) salts[221-223] also afforded cationic species with allylic tins. The possibility was indicated that Tl(III) salts, soft Lewis acids, oxidized the allylic tin *via* π-coordination and a SET path then formed an allylic thallium(III) compound (Scheme 49b). These umpolung reactions provide novel transmetalation reactions.

Scheme 49.



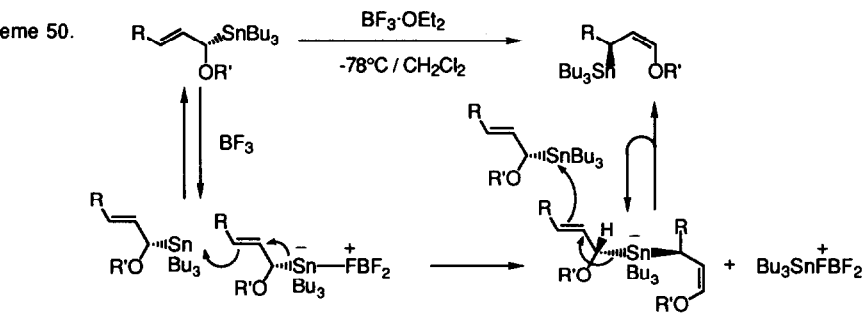
When the transmetalation reactions are undesirable side reactions, the overall process can become complicated. An effort to suppress such reactions was made in some cases ((*i*-PrO)$_3$TiCl, $MeSiCl_3$ as a Lewis

acid).[127,135,224] By controlling the transmetalation reaction, allylic tins can be excellent precursors of various allylic metal reagents possessing characteristic reactivities.

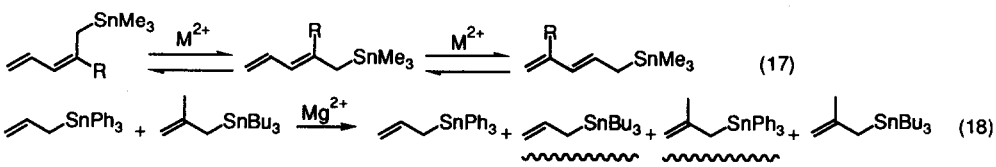
3.2. *Isomerization of Allylic Tin Compounds*

There is another case of interaction between Lewis acids and allylic tins, where isomerization of allylic tins proceeds without transmetalation. It has been shown that non-transmetalating Lewis acids, typically BF_3-OEt_2 and $AlCl_3$, promote 1,3-tin migration[22,58,197,209] and *Z/E* isomerization of crotyl-type tin compounds (eq. 15).[34,112] This explains the partial formation of the linear α-adduct in the reaction between an aldehyde and crotyltin;[34,94] a small amount of the isomerized 1-methylallyltin can react at its γ-position (eq. 16). Thus, it is unnecessary to consider *in situ* formation of new reagents. 1-Alkoxyallyltins also underwent complete 1,3-tin migration with BF_3-OEt_2 giving (*Z*)-3-alkoxyallyltins preferentially.[39,225] This migration path was investigated in some detail by the use of optically active 1-alkoxyallyltins.[64,226,227] Analysis of the absolute configuration of the isomerized 3-alkoxyallyltins, crossover experiments and kinetic data led to the conclusion that the isomerization proceeded by the intermolecular *anti*-S_E' pathway. This was initiated by the coordination of a fluorine atom of BF_3 to the tin atom (Scheme 50).[226] Silyl triflates also promoted the isomerization.[227] These optically active allylic tins, both parent and isomerized, are of course important for asymmetric synthesis.[228]

Scheme 50.



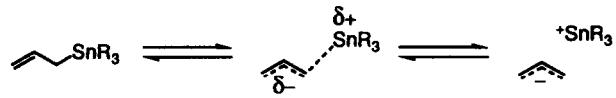
Tin migration is also known in the reaction of pentadienyltins in the presence of alkaline earth perchlorates in acetonitrile (eq. 17).[129] In this case, the migration was [1,5] and intermolecular stannyl group transfer was suggested. Allylic tins were also isomerized similarly (eq. 18). The metal ion was considered as a π-coordinating Lewis acid because the isomerization was inhibited in the coordinative solvents ethanol and THF. The isomerized pentadienyltins were trapped by 1,4-naphthoquinone as Diels-Alder adducts.



It should be noted that similar isomerization has been brought about in the presence of Me_3SnCl[229] and in

polar solvents (alcohol, pyridine, dimethyl sulfoxide).[229-233] It was reported that 1-methylallyltin preferentially isomerized to (*Z*)-crotyltin.[229] This common feature can be understood in terms of the enhanced polarity of the C-Sn bond (Scheme 51).

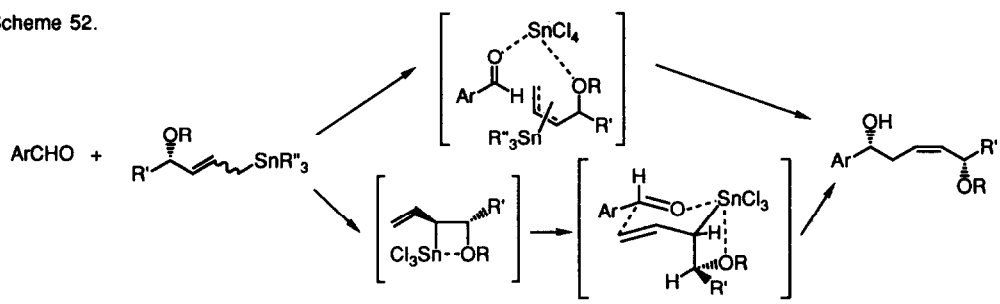
Scheme 51.



3.3. *Other Interactions between Lewis Acids and Allylic Tins*

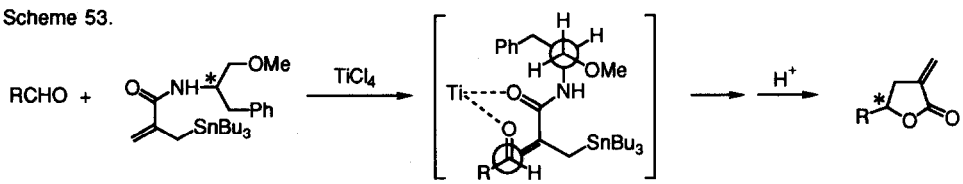
Coordination of a Lewis acid to the substituent on an allylic tin is another type of interaction between Lewis acids and allylic tins. Both (*E*)- and (*Z*)-4-alkoxy allylic tins as well as the regioisomeric 1-alkoxymethylallyltins were allowed to react with aldehydes in the presence of $SnCl_4$ to afford (*Z*)-alkoxy homoallyl alcohols (Scheme 52).[234-236] When chiral reagents were employed high levels of asymmetric induction were realized.[236] The use of $BF_3{\cdot}OEt_2$ or $MgBr_2{\cdot}OEt_2$ was reported to cause γ-addition of 4-alkoxyallyltin.[237] This unusual selectivity was attributed to bidentate $SnCl_4$ coordination with both the aldehyde and the ethereal oxygen of the reagent[234] and transmetalation resulting in the formation of allyl-rearranged (1-alkoxy-alkylallyl)trichlorotin, which should react *via* a six-membered transition state.[236]

Scheme 52.

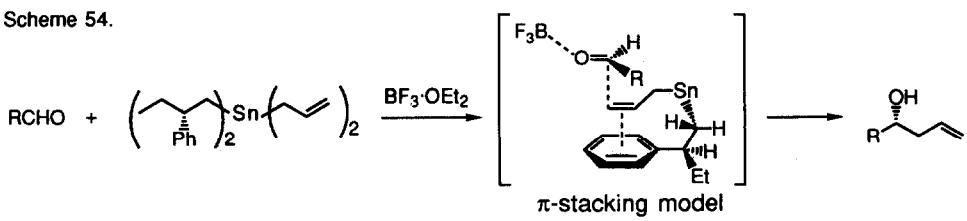


It was reported that allylic tins possessing an optically active amide moiety produced rather high asymmetric induction from the tin reagents.[238] $TiCl_4$ gave the best result because concomitant coordination of $TiCl_4$ to the both carbonyl groups of the aldehyde and the amide moiety could control the enantioselectivity (Scheme 53). In comparison, the use of an allyltin ligated by optically active hydrocarbons in a $BF_3{\cdot}OEt_2$-

Scheme 53.



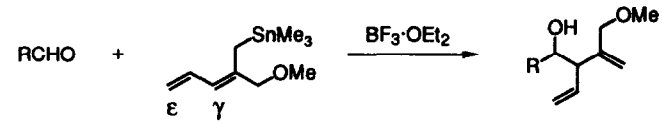
Scheme 54.



π-stacking model

mediated reaction led to a moderate degree of asymmetric induction.[239,240] $SnCl_4$ and $TiCl_4$ promoted complex side reactions. π-Stacking between the phenyl ring on the ligand and the allyl moiety accounted for the enantioselectivity (Scheme 54).[240]

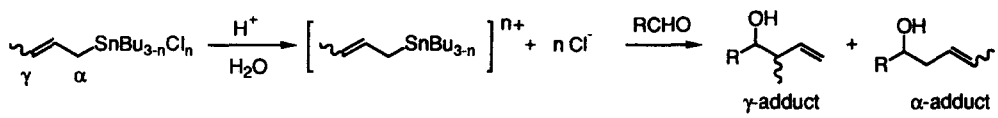
There is an example of regiocontrol where Lewis acid-coordination to an ethereal oxygen atom on pentadienyltin shifted reaction from the ε-position to the γ-position.[241] Coordinated Lewis acid seems to play a role in bringing the both reaction centers closer.



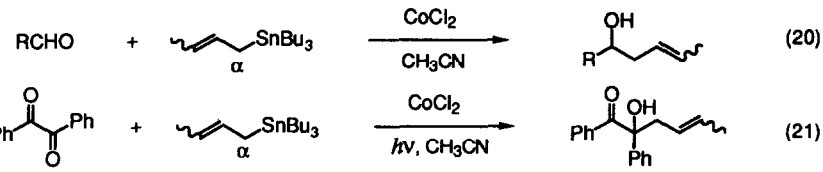
(19)

Another interesting case of activation of allylic tins is that of allylic butyltin halides by protic acids in aqueous media.[242,243] Tin reagents were activated as allylic butyltin cations formed by Cl^- dissociation in the solution (Scheme 55) and the electrophilicity of the tin atom influenced the reaction course. The more positive the tin center was, the more preferentially formed was the α-adduct.[201,243] Protons can also activate aldehydes by protonation of their carbonyl oxygen.

Scheme 55.



It has been reported that $CoCl_2$[244] promotes α-selective allylation of aldehydes with crotyltin.[245] Similarly, the photochemical reaction of benzil (eq. 21) has been observed .[246] Considering the mild Lewis acidity of $CoCl_2$, interaction with allylic tins is more probable than with carbonyl compounds.



(20)

(21)

4. CONCLUSIONS

We have reviewed the developing reaction system of allylic tins mainly from the viewpoint of the roles of Lewis acids. The characters of applied Lewis acids, such as coordinating strength, number of acceptor sites, charge, hardness and softness, steric bulk, transmetalating ability, electron-deficiency, reactivity of the ligands, etc. all influence the roles which they play. On the basis of newly acquired knowledge in the fields of both organic and inorganic chemistry, we can begun to understand the reactions of allylic tin-Lewis acid-substrate systems, to appreciate the remarkable influence of solvents or reaction media, and to anticipate new discoveries and wide applications of these systems

Acknowledgement—I thank Professor W. D. Ollis for inviting me to write this Report and also for his linguistic advice.

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