

Do Metal Perchlorates act as a Conventional Lewis Acid in the Allylstannation of Aldehydes? †

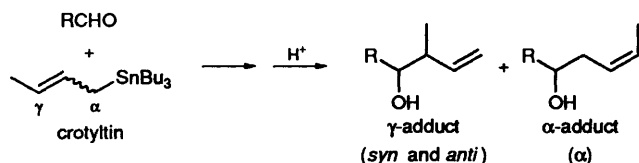
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Lithium, magnesium and calcium perchlorates are found to promote the addition of allylic tin compounds to aldehydes *via* a six-membered cyclic transition state, although not acting as a conventional Lewis acid like BF_3 .

In an earlier report,¹ we described how allylic tin compounds in the presence of various metal perchlorates underwent efficient regio- and stereo-chemical isomerization. In this connection, there has been recent interest in the ability of lithium perchlorate in ether to promote a variety of reactions,² although its role is unclear; variously, the latter has been suggested to be: to stabilize a polar transition state,³ to increase internal solvent pressure,⁴ or to act as a Lewis acid.⁵ We have now examined the reaction between allylic tins and aldehydes in ether in the presence of metal perchlorates in an attempt to elucidate their role.

First, we examined the reaction of allyltributyltin with benzaldehyde in ether in the presence of LiClO_4 ‡ (Table 1). With a high concentration of the salt (4 mol dm^{-3} ; *ca.* 20 mol equiv. of LiClO_4 to the aldehyde), allylstannation proceeded rather well (entry 2). Interestingly, $\text{Mg}(\text{ClO}_4)_2$ §, which is scarcely soluble in ether, was also found to be effective (entry 3); in this case, *ca.* 2 equiv. was enough to increase the yield. As for other group 2 metal perchlorates, $\text{Ca}(\text{ClO}_4)_2$ gave a similar result (entry 4), but $\text{Ba}(\text{ClO}_4)_2$ promoted no reaction (entry 5).



Although crotyltributyltin (but-2-enyltributyltin), to our disappointment, was found to give a much decreased yield compared with allyltin, its diastereoselectivity was of interest (Table 2). Thus, while (*E*)-crotyltin preferentially afforded the corresponding *anti*-homoallyl alcohol (**I**) in LiClO_4 -promoted reactions with aromatic aldehydes (entries 1–3), the *Z*-compound afforded the *syn*-product (**II**) with moderate selectivity ¶ (entry 4). Similar yields and stereospecificity by (*E*)- and (*Z*)-crotyltins were shown in the presence of 1.5 equiv. of $\text{Mg}(\text{ClO}_4)_2$ (entries 6–10); $\text{Ca}(\text{ClO}_4)_2$ also showed a similar result (entry 12). This *anti*-selectivity of (*E*)-crotyltin was the reverse of that shown by a typical Lewis acid (BF_3); *syn*-selectivity was observed even in diethyl ether (entry 13). With aliphatic aldehydes, much lower *syn*-selectivity was observed

† This work was partly presented at the 63rd Annual Meeting of the Chemical Society of Japan, March 1992, Osaka and at the 42nd Symposium on Organic Reactions, November 1992, Osaka.

‡ Lithium perchlorate-promoted addition of allyltin to α -alkoxy aldehydes was reported by Grieco *et al.*,⁶ but no mechanistic discussion was given.

§ $\text{Mg}(\text{ClO}_4)_2$ used in this experiment contained *ca.* 30% water.

¶ Considerable isomerization from (*Z*) to (*E*)-crotyltin¹ was observed in entries 4 and 8.

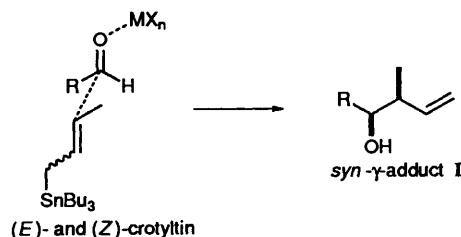
Table 1 Metal perchlorate-promoted reaction of allyltin towards benzaldehyde

Entry	Metal perchlorate (equiv.)	Yield (%) ^a
1	None	0
2	LiClO_4 (20)	55
3	$\text{Mg}(\text{ClO}_4)_2$ (2)	80
4	$\text{Ca}(\text{ClO}_4)_2$ (2)	82
5	$\text{Ba}(\text{ClO}_4)_2$ (2)	Trace

^a Isolated yield of 1-phenylbut-3-en-1-ol.

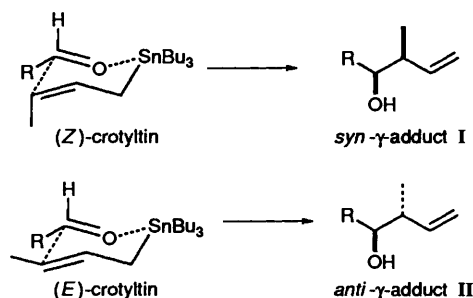
for both LiClO_4 - and $\text{Mg}(\text{ClO}_4)_2$ -promoted reactions (entries 5 and 11) compared with that for BF_3 -promoted reaction (entry 14).

Although in the Lewis acid-promoted reaction, both (*E*)- and (*Z*)-crotyltins are known to afford a *syn*-product *via* an extended acyclic transition state⁷ (Scheme 1), it is not possible



Scheme 1

to give a complete explanation for the role of the perchlorates in the above reactions in terms of the Lewis acidity of their metal cations. The stereoselectivity and stereospecificity observed in the present work parallels that observed in the thermal reaction of crotyltin, where the cyclic six-membered transition state (Scheme 2) is believed to occur.⁸ In such an explanation,



Scheme 2

account should be taken of the contribution of the more congested cyclic transition state, stabilized by the metal

Table 2 Metal perchlorate-promoted reaction of crotyltin^a toward aldehydes (RCHO)

Entry	Metal perchlorate (equiv.)	R	Product distribution			Total yield (%)
			I (<i>syn</i>)	II (<i>anti</i>)	α^b	
1	LiClO ₄ (20)	<i>p</i> -MeC ₆ H ₄	13	57	30	19
2		C ₆ H ₅	14	64	22	15
3		<i>p</i> -O ₂ NC ₆ H ₄	34	58	8	17
4 ^c	Mg(ClO ₄) ₂ (1.5)	<i>p</i> -O ₂ NC ₆ H ₄	56	39	5	18
5		C ₇ H ₁₅	26	23	51	22
6		<i>p</i> -MeC ₆ H ₄	26	59	15	20
7		C ₆ H ₅	24	68	8	16
8 ^c		C ₆ H ₅	50	41	9	13
9		<i>p</i> -MeO ₂ CC ₆ H ₄	22	75	3	12
10		<i>p</i> -O ₂ NC ₆ H ₄	29	71	Trace	9
11		C ₇ H ₁₅	47	37	16	18
12	Ca(ClO ₄) ₂ (2)	C ₆ H ₅	22	57	21	16
13	BF ₃ ·OEt ₂ (2)	C ₆ H ₅	49	18	33	95
14		C ₇ H ₁₅	79	16	5	75

^a (*E*)-Crotyltin (*E/Z* > 9/1) was used unless otherwise noted. ^b The double bond geometry was *Z*. ^c (*Z*)-Crotyltin (*E/Z* = 3/7) was used.

perchlorates, not acting as a conventional Lewis acid. The marked decrease in reactivity of crotyltin also compares with the thermal (high pressure) reaction.⁹

From a competitive experiment, the reactivity toward benzaldehyde of (2-*tert*-butylallyl)tributyltin was found to be nearly equal to that of allyltributyltin in the typically Lewis acid-promoted reaction. In contrast, in the metal perchlorate-promoted reactions, the former was found to be less than one tenth (LiClO₄) and *ca.* a quarter [Mg(ClO₄)₂] of the latter; it seems that in a congested cyclic transition state, the steric bulk of Bu^t is likely to have more influence than in a looser acyclic one.

In conclusion, the role of metal perchlorates in our work is not adequately explained in terms of conventional Lewis acid-like behaviour, polar effects or internal pressure being more important in promoting the reactions.* Even if they should activate aldehydes by coordination, it is not strong enough to exclude allyltin coordination to the aldehyde.

Experimental

Typical Reaction Procedure.—A mixture of an aldehyde (0.2 mmol), an allylic tin reagent (0.3 mmol) and an appropriate perchlorate (or BF₃·OEt₂) (indicated amount) in diethyl ether (1 cm³) was stirred vigorously at room temperature in a capped vial for 1 day (for 5 h in case of BF₃·OEt₂) after which it was poured into a 10% aqueous KF and stirred for 30 min. The mixture was extracted with ether and the extract was dried (Na₂SO₄) and concentrated under reduced pressure. The

product was purified by TLC on silica gel (hexane containing 10–15% diethyl ether).

Competitive Experiment.—Benzaldehyde (0.2 mmol), allyltributyltin (0.3 mmol) and (2-*tert*-butylallyl)tributyltin (0.3 mmol) were subjected to a procedure similar to that described above and the product composition was determined by ¹H NMR (270 MHz) analysis.

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* The role of metal perchlorates was partly affected by the properties of the aldehydes used and the quantity of the perchlorate employed. Even in the reaction of crotyltin with benzaldehyde, a large excess of Mg(ClO₄)₂ (7.5 equiv.) resulted in decreased *anti*-selectivity (*syn/anti* = 58/42) and formation of considerable amounts of α -adduct (α) (γ/α = 45/55), though with a higher combined yield of the products (90%). In addition, metal perchlorates promote 1,3-migration of the tin atom.¹