

## Unusual $\epsilon/\gamma$ -Regiospecificity of (*E/Z*)-Pentadienyltin in the Lewis Acid-promoted Reaction with an Aldehyde

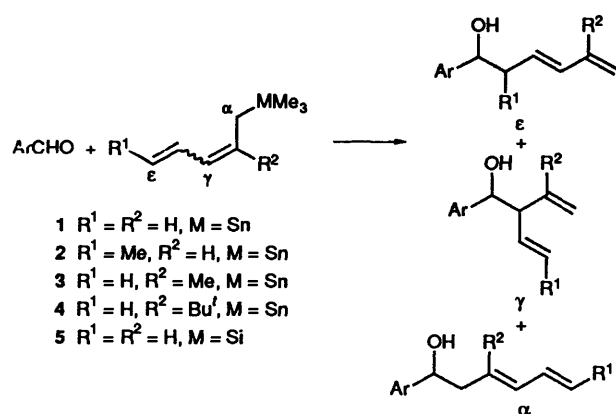
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In the Lewis acid-promoted reaction between pentadienyltin (PDT) and an aldehyde, (*E*)- and (*Z*)-PDTs exhibit opposite regioreactivities: (*E*)-PDT reacts at the terminal  $\epsilon$ -position and (*Z*)-PDT at the internal  $\gamma$ -position.

Pentadienyl-tin (PDT)<sup>1</sup> and -silane (PDS)<sup>2</sup> are stable pentadienyl nucleophiles which are important reagents for the introduction of a conjugated diene moiety into electrophiles.<sup>3</sup> As vinylogues of allyl-tin and -silane possessing an extended conjugated system, PDT and PDS react at their terminal  $\epsilon$ -position;<sup>2,4</sup> this behaviour parallels that of their allylic congeners which react at their terminal  $\gamma$ -position *via* an  $S_E'$  pathway in Lewis acid-promoted addition to aldehydes.<sup>5</sup>

This seemingly common feature occurs, however, only as long as the PDT has *E*-geometry. We describe herein that (*Z*)-PDT<sup>1</sup> preferentially added at the internal  $\gamma$ -position to aldehydes in the presence of an appropriate Lewis acid (Scheme 1).



Scheme 1 Reagents and conditions: Lewis acid,  $-78^\circ C$ ,  $CH_2Cl_2$ ; Ar = *p*-nitrophenyl

When (*E*)-penta-2,4-dienyltin, (*E*)-1, was allowed to react with *p*-nitrobenzaldehyde in the presence of a Lewis acid,† addition at the  $\epsilon$ -position of 1 preferentially occurred (Table 1, entry 1) as already described.<sup>4</sup> A similar result, but with a little less  $\epsilon$ -preference, was observed for (*E*)-hexa-2,4-dienyltin, (*E*)-2 (entry 3).

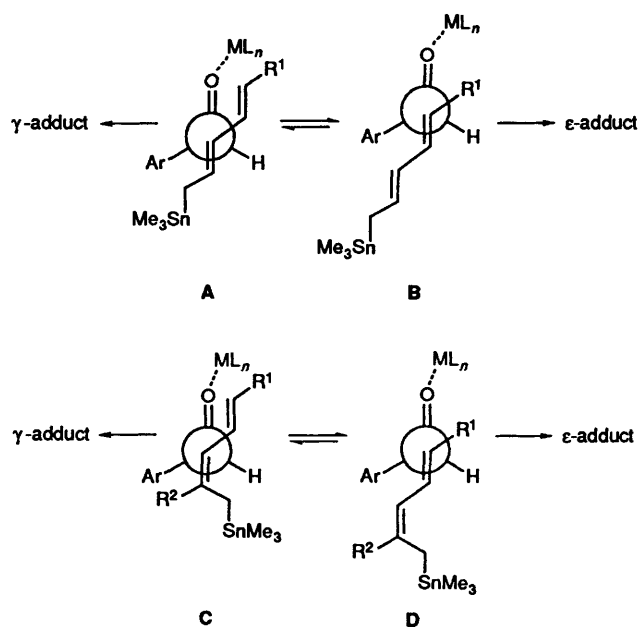
In contrast, and to our surprise, the corresponding (*Z*)-isomers (*Z*)-1 and (*Z*)-2, under the same conditions were found to undergo preferential addition at their  $\gamma$ -positions (entries 2 and 4). This unusual  $\gamma$ -preference also occurred with high selectivity in the reaction of 2-substituted PDT, (*Z*)-2-methylpentadienyltin, (*Z*)-3, and the aldehyde (entry 5).

† Reactive *p*-nitrobenzaldehyde was used as a substrate. A less reactive aldehyde such as cyclohexanecarbaldehyde did not accurately reflect the reactivity of (*Z*)-PDTs, its slower reaction causing concomitant Lewis acid-catalysed isomerizations from (*Z*)-PDT to (*E*)-PDT.<sup>6</sup>

However, (*Z*)-2-*tert*-butylpentadienyltin, (*Z*)-4, exhibited  $\epsilon$ -selectivity rather than  $\gamma$ -selectivity (entry 6).

In comparison, and as reported earlier,<sup>2d</sup> when the nucleophile was homologous PDS 5, both (*E*)- and (*Z*)-isomers exhibited  $\epsilon$ -selectivity to give a conjugated diene (entries 7 and 8).

The above results highlight the unexpectedly high and previously neglected reactivity at the  $\gamma$ -position of (*Z*)-PDTs. Tin is more electropositive than silicon, so PDTs are expected to react more anion-like than PDSs. In fact, similar regioselectivity was observed in the protonation of anionic pentadienyllithiums; (*Z*)- or 'U'-ones gave 1,4-dienes and (*E*)- or 'W'-ones gave conjugated 1,3-dienes preferentially, presumably owing to electronic factors.<sup>7</sup> Consequently, (*Z*)-PDTs, (*Z*)-1–3, afforded the  $\gamma$ -adducts *via* the antiperiplanar transition state C<sup>8</sup> shown in Scheme 2. In contrast, when (*E*)-PDTs were employed, the



Scheme 2

transition state A, which would give  $\gamma$ -adducts, was disfavoured as a result of electronic and steric features, whilst the favoured and less congested transition state B afforded the  $\epsilon$ -adducts. Even in the reaction of (*Z*)-PDT, steric hindrance arising from a bulky 2-substituent (e.g.  $R^2 = Bu^t$ ) gave rise to transition state D and afforded the  $\epsilon$ -adduct. For PDS, a less anionic and less reactive nucleophile than PDT, the electronic factor may be less dominant and the transition state may be more product-

**Table 1** Lewis acid-promoted reaction of (*E*)- and (*Z*)-pentadienyl-tins and -silanes

Entry	PDT (PDS)	R <sup>1</sup>	R <sup>2</sup>	M	Lewis acid	Product ratio			Total yield (%)
						ε	γ	α	
1	( <i>E</i> )-1	H	H	Sn	TiCl <sub>4</sub> -Et <sub>2</sub> O <sup>a</sup>	79	21	—	92
2	( <i>Z</i> )-1	H	H			24	76	—	94
3	( <i>E</i> )-2	Me	H		BF <sub>3</sub> ·OEt <sub>2</sub>	60 <sup>b</sup>	38 <sup>c</sup>	2	98
4	( <i>Z</i> )-2	Me	H			25 <sup>b</sup>	74 <sup>c</sup>	1	95
5	( <i>Z</i> )-3	H	Me			14	82 <sup>b</sup>	4	97
6	( <i>Z</i> )-4	H	Bu <sup>f</sup>			88	3 <sup>c</sup>	9	89
7	( <i>E</i> )-5	H	H	Si		100	0	0	45
8	( <i>Z</i> )-5	H	H			100	0	—	59

<sup>a</sup> Et<sub>2</sub>O (ca. 2 equiv.) was added to suppress transmetallation. <sup>b</sup> One diastereoisomer (probably *syn*-isomer) was selectively formed. <sup>c</sup> Diastereoisomeric ratio was not determined.

like, the sterically more congested γ-adduct thus being disfavoured regardless of the double bond geometry.\*†

So far, the regioselectivity of *E/Z*-pentadienyl metal reagents seems to have been neglected, that described here of PDTs appearing to be the first example reported.<sup>10</sup>

### Experimental

**Typical Reaction Procedure.**—To a stirred, cooled (−78 °C) solution of an aldehyde (0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added a Lewis acid (0.6 mmol) under nitrogen. After a few minutes, PDT (0.45 mmol) was added. When the reaction was complete, it was quenched with 2 mol dm<sup>−3</sup> hydrochloric acid. The resulting mixture was extracted with ether. The organic layer was washed with saturated aqueous NaHCO<sub>3</sub> and brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The products were isolated by TLC.

\* In the reaction of (*Z*)-PDS with acyl chlorides, ready formation of γ-adducts was reported.<sup>9</sup> Steric repulsion in the (*Z*)-diene was considered to cause insufficient conjugation of it, thus limiting the ε-attack.

† No Lewis acid-catalysed isomerization of PDS was observed.

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