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STEREOSELECTIVE ALDOL CONDENSATIONS OF ORGANOTIN REAGENTS WITH ALDEHYDES

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Abstract—The reaction of the enolstannanes of cyclohexanone or propiophenone with various aldehydes under kinetic control (−78°) gave predominately the *threo* aldols, diastereoselectivity as high as 95:5 being achieved. At higher temperatures (+45°) predominate *erythro* selectivity was observed. The enolstannane of propiophenone exists as an equilibrium mixture of O–Sn (probably the *E*-isomer) and C–Sn derivatives. Reaction at −78° takes place rapidly with the O–Sn enolate, further reaction requiring isomerization of the C–Sn to the O–Sn enolate. The Pd catalyzed condensation of cyanomethyltributyltin with reactive aldehydes, such as nitrobenzaldehydes, took place at ambient temperatures in polar solvents to give high yields of condensation products. No reaction occurred with aldehydes such as benzaldehyde. Only low stereoselectivity (10–34% ee) was observed when (−) DIOP or (−)BPPM were utilized as chiral phosphine ligands.

The aldol condensation reaction is one of the most straight-forward methods of generating a C–C bond and at the same time constructing a framework with an oxygen functionality in a 1,3-relationship. The importance of this reaction in the synthesis of macrolide and ionophore antibiotics has stimulated activity in the search for aldol condensation reactions that are highly diastereoselective and enantioselective.[1]

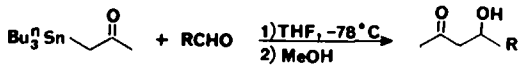
Organotins undergo electrophilic cleavage reactions at the Sn–C bond, and therefore could be expected to undergo condensation reactions with aldehydes, either with reactive aldehydes containing a highly electropositive CO carbon or with Lewis acid activation of the CO group. Indeed, allyltins react with highly activated aldehydes showing *threo* selectivity.[2] When the reaction is carried out at low temperatures in the presence of boron trifluoride,[3] tributylcrotyltin yields the *erythro* product, regardless of the double bond geometry in the tin reagent.[4] Butenylchlorodibutyltin undergoes an aldol-type addition to aldehydes, even in the absence of Lewis acids, however with low diastereoselectivity.[5] In addition, the tin(II) chloride promoted condensation of allyl iodide with aldehydes to yield homoallylic alcohols apparently takes place through an allyltin(IV) intermediate.[6] The cross- and self-aldol condensations between aldehydes and ketones take place at −78° in the presence of an amine and stannous triflate, showing *erythro* selectivity. Presumably this reaction takes place by the *in situ* generation of a tin enolate derivative.[7]

We undertook a study of the aldol condensation reaction of tin enolates with aldehydes, with the expectation that the reaction would be catalyzed by certain Pd(II) (Lewis acid) complexes.[8] Thus, it was hoped that not only would a diastereoselective reaction be achieved but also that a stereoselective synthesis could be effected when the Pd(II) complex contained chiral phosphine ligands. This expectation was supported by the knowledge that enolstannanes serve as nucleophiles in coupling reactions with electrophiles,[9] and that Pd is an effective catalyst in the coupling reactions of organic halides with organotins.[10] In this Pd catalyzed coupling reaction, a key step in the catalytic cycle is a transmetallation reaction in which the bis(triphenylphosphine)-chloroorganopalladium(II) complex acts as an electrophile, cleaving the Sn–C bond. Further, the reaction of tributylacetonyltin, a reagent which contains a C–Sn bond rather than the tin enolate structure, undergoes an uncatalyzed aldol condensation reaction with benzaldehyde at ambient temperature.[11]

While this investigation was in progress, the aldol condensation reaction of aldehydes with tin enolates generated *in situ* was reported[12] to give moderate *erythro* selectivity under kinetic control. These results were surprising since we had observed predominate *threo* selectivity in reactions of various aldehydes at −78° with several tin enolates that had been synthesized and then isolated prior to their reaction.[8]

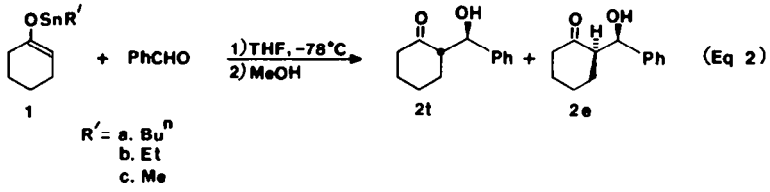
RESULTS AND DISCUSSION

In the aldol condensation reactions of aldehydes with various organotins, the tin reagents were first isolated and purified. Acetonyltributyltin reacted with benzaldehyde or isobutyraldehyde at −78° in the absence of any catalyst to give the aldol condensation product (eqn 1). The rapid, uncatalyzed reaction precluded the possibility that a stereoselective reaction could be effected by a chiral catalyst.



R = Ph, $(CH_3)_2CH$- (Eq 1)

The tin enolate, 1-cyclohexenyloxytributyltin (**1a**) exists primarily as the O-stannane, and is written as such. Although the vinyl proton was apparent in the ^1H NMR spectrum (δ 4.35), and the corresponding proton of the C-stannane was not detected; a weak signal in the IR spectrum at 1720 cm^{-1} could be observed.



1-Cyclohexenyloxytributyltin (**1a**) reacted with benzaldehyde at −78°, also in the absence of catalyst, to give high yields of the aldol condensation product, 2-(hydroxybenzyl)cyclohexanone (**2**, eqn 2). At this temperature the predominant product was the *threo* isomer (**2t**), diastereoselectivity decreasing with increasing temperature (Table 1).[13] At +45°, the erythro isomer (**2e**) predominated. 1-Cyclohexenyloxytriethyltin (**1b**) and 1-cyclohexenyloxytrimethyltin (**1c**) showed higher *threo* selectivity at −78° than the tributyltin analog, both **1b** and **1c** giving a 92:8 ratio of **2t**:**2e**. These results are in contrast to the report[12] that the triphenyltin enolate, formed *in situ* from the reaction of the lithium enolate of cyclohexanone with triphenyltin chloride, reacts with benzaldehyde at −78° to give the *erythro* product, and that tributyl- and trimethyltin enolates of cyclohexanone are nonselective. We were unable to prepare and isolate the pure 1-cyclohexenyloxytriphenyltin derivative. However, in our hands, under reaction conditions in which the 1-cyclohexenyloxytriphenyltin was generated *in situ* from the reaction of the lithium enolate of cyclohexanone and triphenyltin chloride, a 66:34 mixture of *threo* (**2t**) to *erythro* (**2e**) aldol was obtained.

The *threo* and *erythro* assignments were made primarily from the benzylic proton coupling constants of **2t** and **2e** ($J_{H_{ab}}$ = 9.0 and 3.0, respectively), in agreement with those generally observed[14] for *threo* (8–9 Hz) and *erythro* (2–3 Hz) aldols. The diastereomeric aldols, **2t** and **2e**, could be distinguished by reverse phase HPLC. Both the coupling constants for **2t** and **2e** and the retention times on HPLC were compared with authentic samples prepared by an independent method.[14] In addition, the chemical shifts for benzylic protons in **2t** and **2e** (δ 4.85 and 5.35, respectively) matched the authentic samples. The relative ratios of the *threo* and *erythro* aldols were determined, therefore, both by integration of the HPLC and the ^{1}H NMR.

To assess the diastereoselectivity in reactions of aldehydes with acyclic enol stannanes, 1-phenyl-1-propenyloxytributyltin **3a** and 1-phenyl-1-propenyloxytriethyltin **3b** were prepared by the reaction of 1-phenyl-1-propen-1-ol acetate at 0° with tributyltin- and triethyltin methoxide, respectively. Both the O- and C-stannanes were obtained as an equilibrium mixture. The chemical shifts corresponding to the vinyl protons in **3a** and **3b** were observed at δ 5.05, and the corresponding proton of the C-stannane derivatives at δ 2.94 in the ^{1}H NMR spectra. The vinyl proton in **3a** appeared as a quartet (J = 6.84 Hz), similar to that reported.[15] The absorption at 1700 cm^{-1} in the IR spectra of **3a** and **3b**, as well as the signal for the CO carbon in the ^{13}C spectra (δ 199.9), confirmed the presence of the C-stannane in the equilibrium mixture. The ratio of the isomers, O-stannane to C-stannane, 50:50, in deuterochloroform at 25° was obtained by integration of the signals at δ 5.05 and 2.94, respectively. The ratio of the two isomers in tetrahydrofuran either at +25° or at −78° was 10:90 (O–Sn:C–Sn).

Since a single quartet corresponding to the vinyl proton was present in the ^{1}H NMR spectrum of the mixture of O-stannane and C-stannane derivatives of **3a**, assignment of the *E* or *Z* geometry to the enolate was not possible. However, the tributylenolstannane derived from 2-butanone has been reported to be in equilibrium with 77% of the C-stannane derivative (vs O–Sn derivative) and the O-stannane isomer was reported to be exclusively the *E*-isomer.[16] Thus, the O-stannane isomers of **3** have been written as the *E*-isomers, although this could not be experimentally established.

The tin enolates **3a, b** reacted with various aldehydes at −78° with high *threo* selectivity to yield the aldol condensation products (**4**, eqn 3). As was observed for enol stannane **1**, reversal of the diastereoselectivity occured at higher temperatures (Table 2).

The ratio of *threo* aldol **4t** to *erythro* aldol **4e** was determined both by ^{1}H NMR and reverse phase HPLC. The benzylic proton, H_b, of the *threo* aldol (**4t**, R′ = Ph) was observed at δ 5.1 with a coupling constant $J_{H_{ab}}$ of 8.1 Hz. The corresponding chemical shift and coupling constant for the *erythro* aldol (**4e**, R′ = Ph) were δ 5.3 and 3.0 Hz. The relative ratios of **4t** and **4e** were obtained by the integration of the two signals at δ 5.1 and δ 5.3, respectively. The two diastereomers also were distinguished on reverse phase HPLC using an acetonitrile–water solvent system, and the assignment of the peaks were made by comparison with the retention times observed for

Table 1. Condensation of 1-cyclohexenyloxytrialkyltins with benzaldehyde (eqn 2)

Enolstannane 1	T°C/t, h	Yield %	2t	2e
a. R = Bu^n	-78/6	78	80	20
	-45/6	83	77	23
	+45/2	86	23	77
b. R = Et	-78/6	89	92	8
	+45/5	90	30	70
c. R = Me	-78/6	88	92	8

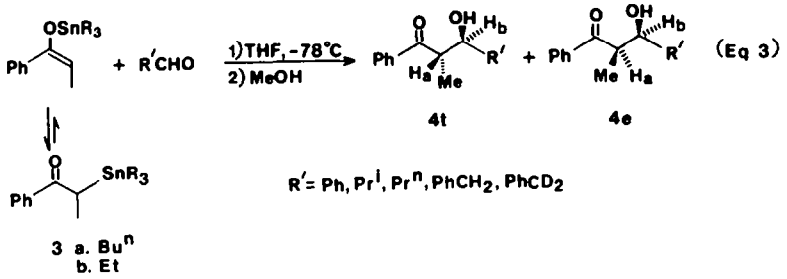


Table 2. Condensation of 1-phenyl-1-propenyloxytrialkyltin (3) with aldehydes to give aldols (4)

Enolstannane, R	Aldehyde, R'	T°(C)[a]	Yield (%)[b]	4t : 4e
3a, Bu^n	Ph	-78	70	88 12
	Pr^i	-78	50	75 25
	Pr^n	-78	70	90 10
	$PhCH_2$	-78	70	95 5
	$PhCD_2$	-78	70	95 5
	$PhCH_2$	+43	80	10 90
	$PhCD_2$	+43	80	10 90
3b, Et	Ph	-78	50	90 10
	Pr^i	-78	48	93 7
	$PhCH_2$	-78	85	84 16

[a]Reaction time 6 h.

[b]Isolated yields.

the pure *threo* aldol (**4t**, R′ = Ph, 9.13 min) and *erythro* aldol (**4e**, R′ = Ph, 7.20 min) obtained by separation of the mixture of diastereomers by radial chromatography.

The coupling constants J_{H_ab} for proton H_b in aldols **4** (R′ = Pr^i, Pr^n, $PhCH_2$) could not be readily determined because of the additional coupling to the protons in the i-propyl, n-propyl, and benzyl groups, respectively. The chemical shifts of H_b in the two diastereomers were not separated sufficiently to allow the determination of the relative ratios of the *threo* and *erythro* aldols. Moreover, the diastereomers could be separated neither by radial chromatography nor by medium pressure liquid chromatography. The two diastereomers could be distinguished, however, by reverse-phase HPLC and the relative ratios of the two diastereomers could be obtained. The assignment of the peaks to the *threo* and *erythro* isomers (Table 2) were made by analogy to the retention times observed for the *threo* and *erythro* aldols, **4t** (R′ = Ph) and **4e** (R′ = Ph), respectively.

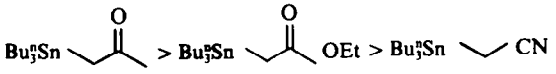
In addition, the condensation reaction of **3a** with 1,1-dideuterophenylacetaldehyde at −78° and +43° gave predominately two different diasteromers, as indicated by their ^{1}H NMR spectra and their retention times on reverse-phase HPLC. The coupling constant J_{H_ab} for aldol **4t** (R′ = $PhCD_2$) at −78° was larger (5.61 Hz) than that observed for aldol **4e** (R′ = $PhCD_2$) (3.17 Hz) obtained at +43°. By analogy to those coupling constants observed for the *threo* and *erythro* diastereomers, the product obtained at −78° was assigned the *threo* isomer (**4t**, R′ = $PhCD_2$) and that obtained at +43° was assigned the *erythro* isomer (**4e**, R′ = $PhCD_2$). Shorter retention times on reverse-phase HPLC were observed for the *erythro* aldols in all examples. This relationship between the *threo* and *erythro* aldols, and their retention times on reverse-phase HPLC was utilized in determining the *threo*: *erythro* ratios.

When the reaction of **3a** with butyraldehyde in tetrahydrofuran at −78° was followed by ^{1}H NMR the signal at δ 5.05, corresponding to the O-stannane isomer disappeared immediately, leaving only the proton at δ 2.94, characteristic of the C-stannane derivative; and the spectrum characteristic of the C-stannane derivative disappeared more slowly. Apparently, the O-stannane is the reactive species, and the isomerization of the C–Sn to the O–Sn derivative at −78° is necessary for the aldol condensation reaction to take place.

In aldol-type condensations under kinetic control, *E*-enolates yield the *threo*-aldol, a consequence ascribed to a chair-like 6-membered transition state.[17] The required *E*-enolate structure is present in the enolstannane of cyclohexanone (**1**) and assumed in the O-stannane derivative of propiophenone (**3**). Condensations between metal enolates and aldehydes under kinetic conditions generally are *erythro*-selective, and a large number of such reactions have been established. Among *threo* and *erythro* aldols, the *threo* aldol generally is the most thermodynamically stable, equilibration to the *threo* product being achieved by a retro-aldol reaction. Thus, the diastereoselectivity at low temperatures to the *threo* aldol and at high temperatures to the *erythro* aldol is unusual. Furthermore, the intermediate *threo* aldol stannane is not converted to the *erythro* aldol stannane at higher temperatures. When the aldol stannane obtained from **1** and benzaldehyde in a 3 h reaction at −78° was not quenched, but was allowed to warm to +45° and remain at this temperature for 3 h, the *threo* to *erythro* ratio obtained was the same (80:20)

as that obtained from the reaction at −78°. The high *threo* selectivity of the reaction between enolstannanes and aldehydes under kinetic conditions classify it as one of the few simple *threo*-selective reactions known.

The reactivity of unsymmetrical organotin reagents, in which one of the organic groups contains an electron withdrawing group attached to the C bonded to Sn, is sensitive to the particular withdrawing group. Thus, although acetonyltributyltin reacts spontaneously with aldehydes at −78°, certain other organotin reagents could be expected to require catalysis. The reaction of ethyl α-tributylstannylacetate with benzaldehyde proceeds only at 80° in the presence of a zinc chloride catalyst,[18] and generally the order of reactivity for simple organostannanes containing α-substituted electron withdrawing groups is:



Cyanomethyltributyltin (**5**) did not react with benzaldehyde in THF at 65°, even in the presence of a benzylchlorobis(triphenylphosphine)palladium(II) catalyst. Low conversions were obtained in a reaction with a reactive aldehyde, *o*-nitrobenzaldehyde in THF. Reagent **5** did react with *o*-nitrobenzaldehyde (**6**) in coordinating solvents such as DMF, DMSO and HMPA at ambient temperature in the presence of the Pd catalyst (eqn 4); low conversions were obtained with benzaldehyde, however (Table 3). The reaction reached 75% conversion in 6 h with equimolar amounts of the two reagents, but >95% conversion was attained in 4 h with a two fold excess of the tin reagent.

Table 3. Condensation of cyanomethyltributyltin with *o*-nitrobenzaldehyde

Solvent	T°C/t (h)	% Conv.
THF	22/48	0[a]
THF	22/48	35
THF	65/20	65
HMPA	22/20	0[a]
HMPA	22/20	80
HMPA	22/15	95[b]
DMF	22/20	70
DMSO	22/20	63
HMPA	22/20	80[c]

[a]No Catalyst. In all other reactions, 6 mole % of benzylchlorobis(triphenylphosphine)palladium(II) was added.

[b]A two-fold excess of tin reagent.

[c]p-Nitrobenzaldehyde (**7b**) was used.

In an effort to obtain an enantioselective reaction several chiral Pd complexes were prepared *in situ* by the reaction of bis(benzonitrile)dichloropalladium(II) with the desired chiral phosphine ligands. The chiral ligands (−)2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane[19] [(−)DIOP] and (−)N-t-butoxycarbonyl-2(*S*),4(*S*)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine[20] [(−)BPPM] gave the highest enantiomeric excess of product **7** of those chiral phosphines used (Table 4). The enantiomeric excess was determined by the reverse-phase HPLC (48:52 acetonitrile:water) of the

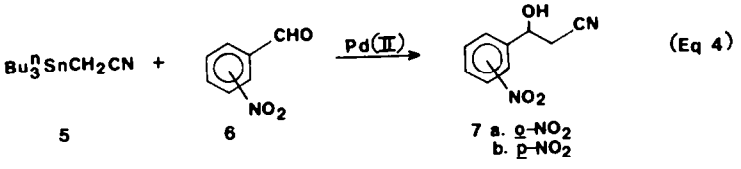


Table 4. Asymmetric synthesis of **7** from the reaction of **5** with **6** in the presence of chiral palladium catalysts

Aldehyde Isomer	Solvent	Time (h)	Phosphine Ligand[a]	% ee[b]
6a	$CHCl_3$	48	(-) DIOP	13
	DMSO	22	(-) DIOP	12
	HMPA	24	(-) DIOP	13
6b	HMPA	24	(-) DIOP	13
6a	HMPA	5	(-) DIOP	34[c]
6b	HMPA	5	(-) DIOP	34
6a	HMPA	23	(-) BPPM	21[c]

[a](-) DIOP = (-) 2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. (-) BPPM = (-) N-t-butoxycarbonyl-2(S),4(S)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine.

[b]Enantiomeric excess determined by reverse-phase HPLC of Mosher's ester.[21]

[c]Enantiomeric excess as determined by ^1H NMR of the ester was considerably lower, giving values of 15% ee (vs. 34) and 10% ee (vs. 21).

diastereomeric esters obtained from 7 and (−)-α-methoxy-α-trifluoromethylphenylacetyl chloride.[21] Also, the OMe protons of the two diastereomeric esters were distinguished in the ^{1}H NMR (δ 3.45 and 3.65), as was the OMe carbon in the ^{13}C spectrum (δ 68.24 and 68.59). The absolute configuration of the enantiomers of 7 could not be established, however. Because of the relatively low asymmetric induction, and the limitation of the reaction to a few reactive aldehydes, reactions of tin reagents that would lead an enantiomeric excess of an aldol containing two chiral centers was not attempted.

EXPERIMENTAL

Tetrahydrofuran (THF) and toluene were freshly distilled from sodium/benzophenone prior to use. Hexamethylphosphoramide was distilled from calcium hydride and stored over 13X molecular sieves under N_2. Chloroform, dimethylformamide and dimethyl sulfoxide were passed through basic alumina prior to the use as solvents in the aldol-type condensation reactions. Reverse-phase HPLC analyses were carried out on Waters model 6000 and M-45 pumps with solvent programmer and a model 440 absorbance detector. A microbondapack-C 18 column was used for reverse-phase HPLC analyses with acetonitrile–water as a solvent mixture. Radial chromatography was carried out with a Chromatotron (Harrison Research Co.). All m.p. and b.p.s are uncorrected. All ^{1}H NMR were obtained on a Varian model EM-360 or a JEOL model FX-100 spectrometer with TMS as an internal standard. ^{13}C NMR were obtained on JEOL model FX-100 spectrometer with $CDCl_3$ as an internal standard. IR spectra were obtained on a Beckman model 4250 spectrometer.

The chiral phosphine ligands, (−) DIOP,[19] and (−) BPPM[20] were prepared according to the reported procedures. Benzylchlorobis(triphenylphosphine)palladium(II)[22] and the tin reagents, 2-propanonetributyltin,[16] and cyanomethyltributyltin[23] were prepared by known procedures.

Preparation of enol acetates.[24] A mixture of 0.10 mol of ketone, 0.20 mol of Ac_2O and 0.2 g (0.001 mol) of *p*-toluenesulfonic acid was heated at the reflux temp. for 12 h. The resulting dark red mixture was cooled to 0°, diluted with pentane and washed with $NaHCO_3$ aq. After the evolution of CO_2 ceased, the pentane layer was separated, and was dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was distilled to obtain the pure product.

The following enol acetates were prepared: 1-Cyclohexene-1-ol acetate[24b] (62%) and 1-phenyl-1-propen-1-ol acetate (30%), b.p. 65° (0.15 mm Hg); ^{1}H NMR ($CDCl_3$) δ 1.66–1.73 (d, 3H, J = 6.84 Hz, –C=CC$\underline{H}_3$), 2.28 (s, 3H, –COC$\underline{H}_3$). 5.77–5.98 (q, 1H, J = 6.84 Hz, –C$\underline{H}$=C–), 7.22–7.34 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ 11.61, 20.66, 112.50, 124.18, 127.85, 128.32, 134.92, 146.83, 168.26. Calc for $C_{11}H_{12}O_2$: C, 74.95; H, 6.86%. (Found: C, 78.48; H, 7.26).

Procedure for the preparation of enol stannanes.[25] To the trialkyltin methoxide at 0° under N_2 was added an equimolar amount of enol acetate dropwise so that temp did not rise above 25°. After the addition was complete, the mixture was allowed to warm up to ambient temp and was allowed to react for 12–15 h. The by-product, methyl acetate, was removed *in vacuo* and the product was collected by distillation under reduced pressure.

The following enol stannanes were obtained by this procedure: 1-Cyclohexeneyloxytributyltin (**1a**)[25] was prepared from the reaction of 1-cyclohexen-1-ol acetate with tributyltin methoxide[26] to give a 70% yield of product. 1-Cyclohexenyloxytriethyltin (**1b**)[27] was similarly obtained from triethyltin methoxide[28] in 55% yield.

1-Cyclohexenyloxytrimethyltin (**1c**) was prepared from the reaction between 2.7g (0.019 mol) of 1-cyclohexen-1-ol acetate and 3.89 g (0.019 mol) of trimethyltin methoxide.[27-29] Trimethyltin methoxide was dissolved in 25 mL of dry toluene, cooled to 0° and the enol acetate was added dropwise. After 12 h, the solvent was removed *in vacuo* and 1.5 g (35%) of the product was collected by bulb-to-bulb transfer at 0.1 mm Hg, as a clear liquid; ^{1}H NMR ($CDCl_3$) δ 0.5 (s, 9H, (C$\underline{H}_3$)$_3$Sn–), 1.5–2.3 (m, 8H), 4.35 (m, 1H, –C$\underline{H}$=C–). The enol stannanes are very unstable and very sensitive to moisture, therefore, elemental analysis or high resolution mass spectral data could not be obtained.

1-Phenyl-1-propenyloxytributyltin (**3a**). This compound was prepared according to the general procedure from the reaction between 2.0 g (0.012 mol) of 1-phenyl-1-propen-1-ol acetate and 3.9 g (0.012 mol) of tributyltin methoxide. The product was collected by distillation under reduced pressure to obtain 3.0 g (50%) as a yellow liquid containing enol stannane and C-Sn derivative, b.p. 135–137° (0.15 mm Hg); ^{1}H NMR ($CDCl_3$) δ 0.8–1.6 (m, 57H), 1.72–1.75 (d, 3H, 6.84 Hz, C=C–(C$\underline{H}_3$)O–Sn), 2.91–2.98 (q, 1H, –CO–C$\underline{H}$(CH$_3$)Sn), 5.04–5.11 (q, 3H, J = 6.80 Hz, –C=C$\underline{H}$CH$_3$), 7.17–7.96 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 9.21, 11.32, 13.48, 13.59, 15.93, 16.34, 27.08, 27.72, 28.13, 31.58 (C-2′, C–Sn), 100.59 (C–2, O–Sn), 125.05, 127.50, 127.62, 128.15, 132.41, 141.40, 155.18 (C–1, O–Sn), 199.90 (C=O, C–1′, C–Sn). Because of the sensitivity of the product to moisture and its instability, elemental analysis and high resolution mass spectral data could not be obtained. The observed ^{1}H NMR data is consistent with that reported.[15]

1-Phenyl-1-propenyloxytriethyltin (**3b**). From the reaction between 1.1 g (0.0063 mol) of 1-phenyl-1-propen-1-ol acetate and 1.6 g (0.0068 mol) of triethyltin methoxide, after distillation under reduced pressure, 1.0 g (30%) of the product as a yellow liquid was obtained. The product was a mixture of C–Sn and O–Sn derivatives, b.p. 100–105° (0.06 mm Hg); ^{1}H NMR ($CDCl_3$) δ 0.8–1.8 (m, 33H), 1.73–1.80 (d, 3H, 6.8 Hz, C=C(CH$_3$)O–Sn), 2.8–3.0 (q, 1H, –CO–C$\underline{H}$(CH$_3$)Sn), 5.0–5.2 (q, 1H, J = 6.84 Hz, –C=C$\underline{H}$·CH$_3$), 7.1–8.12 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 7.05, 7.23, 9.50, 9.80, 11.14, 31.46, 100.35 (C–2, O–Sn), 124.16, 124.76, 127.45, 128.03, 132.29, 141.10, 155.00 (C–1, O–Sn), 199.73 (C=O, C–1′, C–Sn). Because of the instability of the compound analytical data could not be obtained.

1,1-Dideuterophenylacetaldehyde. A mixture of 4.0 g (0.033 mol) of phenylacetaldehyde in 25 mL of dry THF, 20 mL of D_2O and a few drops of HCl was heated at the reflux temp. for 12 h. The resulting mixture was cooled, extracted with ether and the organic layer was washed successively with $NaHCO_3$ aq, water and brine solns. The organic layer was dried over $MgSO_4$, the solvent was removed on a rotary evaporator and the product was collected by distillation under reduced pressure to afford 2.0 g (50%) of 1,1-dideuterophenylacetaldehyde, b.p. 36° (3 mm Hg); IR (neat) 2760 cm^{-1} (–CO–H), 2710 cm^{-1} (C–D), 1725 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 7.09–7.34 (m, 5H, Ar), 9.66 (s, 1H, O=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) 49.88(m), 126.98, 128.55, 129.20, 131.53, 198.79 (C=O).

Procedure for the condensation of enol stannanes with aldehydes. To a soln of 1 mmol of aldehyde in 1 mL of dry THF at −78° was added 1 mmol of enol stannane in 1 mL of THF. The mixture was allowed to react for 5–7 h at −78° after which it was quenched with cold MeOH, poured into water at ambient temp and stirred for 15 min. The product was extracted with ether and the extract was dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was analyzed by ^{1}H NMR and reverse-phase HPLC. The pure products were obtained either by gravity column chromatography or by radial chromatography. The reactions at higher temps were carried out in a similar fashion.

2-(Hydroxyphenylmethyl)cyclohexanone

Erythro, Isomer (**2e**). This compound was prepared from the reaction between 0.4 g (0.001 mol) of 1-cyclohexenyloxytributyltin and 0.096 g (0.001 mol) of benzaldehyde at

+45°. The residue obtained after workup was analyzed by reverse-phase HPLC (acetonitrile–water: 45–55, 2 mL/min). Retention time 9.5 (e), 10.65 (t). The residue was purified by column chromatography to yield 0.13 g (65%) of the product as a white solid which was crystallized from ether, m.p. 105–107° [lit.[14] m.p. 105–107°]; ^{1}H NMR ($CDCl_3$) δ 1.4–2.6 (br m, 9H), 5.35 (dd, 1H, d on D_2O wash, J = 3.0 Hz, –CH–Ph), 7.3 (s, 5H, Ar).

2-(*Hydroxyphenylmethyl*)*cyclohexanone*

Threo Isomer (**2t**). This compound was obtained from the reaction between 0.40 g (0.0010 mol) of 1-cyclohexenyloxytributyltin and 0.096 g (0.0010 mol) of benzaldehyde at −78°. The residue before purification was analyzed by reverse-phase HPLC (acetonitrile-water: 45–55, 2 mL/min.) Retention time 9.5 (e), 10.65 (t). The residue was then purified by column chromatography (silica gel, 10% EtOAc–hexane) to afford 0.15 g (75%) of **2t** as a white solid which was crystallized from hexane–ether, m.p. 76–78° [lit.[14] m.p. 74–75°]; ^{1}H NMR ($CDCl_3$) δ 1.40–2.60 (br m, 9H), 4.1 (d, 1H, OH), 4.85 (dd, d on D_2O wash, 1H, J = 9.0 Hz, –CH–Ph), 7.3 (s, 5H, Ar).

Compound **2t** also was prepared from the reaction of 0.096 g (0.0010 mol) of benzaldehyde with 0.31 g (0.0010 mol) of 1-cyclohexenyloxytriethyltin or 0.27 g (0.0010 mol) of 1-cyclohexenyloxytrimethyltin at −78°. The residue was analyzed by reverse-phase HPLC as above and was then purified to afford 0.15 g (75%) and 0.16 g (80%) of the product for triethyl- and trimethyl enol stannanes, respectively.

1,3-*Diphenyl*-3-*hydroxy*-2-*methyl*-1-*propanone* (**4t**, **4e**, R′ = Ph)

From the reaction between 0.42 g (0.0010 mol) of 1-phenyl-1-propenyloxytributyltin and 0.096 g (0.0010 mol) of benzaldehyde, according to the general procedure, a mixture of *erythro* and *threo* isomers was obtained. This mixture was analyzed by reverse-phase HPLC (acetonitrile–water: 45–55, 2 mL/min), Retention time 7.36 (**4e**), 9.36 (**4t**). The residue was purified by radial chromatography (silica gel, 15% ethyl acetate–hexane) to afford 0.17 g (70%) of the *threo* isomer (**4t**), as a clear viscous liquid, IR (neat) 3400–3200 cm^{-1} (OH), 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 0.98–1.06 (d, 3H, J = 7.32 Hz, –CCH$_3$–), 3.13–3.17 (d, 1H, J = 3.11 Hz, –OH), 3.67–3.87 (m, 1H), 4.90–5.02 (dd, d on D_2O wash, 1H, J = 8.1 Hz), 7.23–8.00 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 15.70, 47.98, 76.71, 126.57, 127.68, 128.26, 128.43, 133.05, 136.67, 142.10, 204.51 (C=O). This compound was identical to an authentic sample prepared by an independent method[14] by comparison of ^{1}H NMR.

Compound **4t** also was prepared by the condensaion of 0.34 g (0.0010 mol) of 1-phenyl-1-propenyloxytriethyltin, with 0.096 g (0.0010 mol) of benzaldehyde at −78°. Upon purification as above 0.17 g (72%) of the product **4t** was obtained.

2,4-*Dimethyl*-3-*hydroxy*-1-*phenyl*-1-*pentanone* (**4**, R′ = Pr^i)

This compound was prepared from the condensation of 1-phenyl-1-propenyloxytributyltin with 0.072 g (0.0010 mol) of isobutryaldehyde. The crude product was analyzed by reverse-phase HPLC (acetonitrile–water: 31–69, 2 mL/min), Retention time 14.70 (e), 19.65 (t). The crude product was purified by radial chromatography (silica gel, 20% EtOAc–hexane) to yield 0.10 g (50%) of the product, IR (neat) 3350–3100 cm^{-1} (OH), 1700 cm^{-1}(C=O); ^{1}H NMR ($CDCl_3$) δ 0.9–1.0 (d, 6H), 1.20–1.22 (d, 3H), 1.25–1.28 (br m, 1H), 3.5–3.8 (m, 2H), 7.3–8.1 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.96, 18.91, 30.82, 42.03, 76.59, 125.95, 128.20, 128.55, 133.11, 135.79, 205.33 (C=O). This compound was identical to an authentic sample prepared by an independent method[14] by comparison of the ^{1}H NMR spectrum.

1,4-*Diphenyl*-3-*hydroxy*-2-*methyl*-1-*butanone*

Erythro Isomer (**4e**, R′ = PhCH$_2$). This compound was prepared from the condensation of 0.42 g (0.0010 mol) of 1-phenyl-1-propenyloxytributyltin and 0.12 g (0.0010 mol) of phenylacetaldehyde at +45°. The crude product was analyzed by reverse-phase HPLC, (acetonitrile–water: 40–60, 2.0 mL/min). Retention time 15.50 (e), 17.10 (t). The residue was purified by radial chromatography (silica gel, 15% ethyl acetate–hexane) to yield 0.18 g (70%) of the *erythro* isomer. The product was crystallized from ether, m.p. 105–106°; IR (neat) 3400–3200 cm^{-1} (O–H), 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.25–1.32 (d, 3H, J = 7.32 Hz, C–CH$_3$), 2.75–2.83 (d, 2H, J = 6.34 Hz, –CH$_2$–Ph), 2.97–3.45 (m, 1H, CH–CO), 4.16–4.33 (m, 1H, CH–O), 7.17–8.02 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.49, 40.62, 43.60, 72.62, 126.22, 128.15, 128.38, 129.03, 129.84, 133.05, 135.56, 138.01, 204.57 (C=O).

1,4-*Diphenyl*-3-*hydroxy*-2-*methyl*-1-*butanone*

Threo Isomer (**4t**, R′ = PhCH$_2$). This compound was prepared from the reaction between 0.42 g (0.0010 mol) 1-phenyl-1-propenyloxytributyltin and 0.12 g (0.0010 mol) of phenylacetaldehyde at −78°, according to the general procedure. The residue was purified by radial chromatography (silica gel, 15% ethyl acetate–hexane) to afford 0.17 g (67%) of the product as a white solid, which was crystallized from hexane, m.p. 81.5–82.5°; IR (nujol) 3400–3200 cm^{-1}. (OH), 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.25–1.30 (d, 3H, J = 7.1 Hz, C–CH$_3$), 2.81–2.90 (d, 2H, J = 7.57 Hz, –CH$_2$–Ph), 3.48–3.62 (m, 1H, CH–CO–), 3.69–4.11 (m, 1H, –CH–CH$_2$–), 7.18–7.94 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.34, 41.50, 44.36, 75.19, 126.22, 128.20, 128.44, 129.14, 133.11, 136.38, 138.19, 205.10 (C=O): Calc for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. (Found: C, 80.40; H, 7.23).

4,4-*Dideutero*-1,4-*diphenyl*-3-*hydroxy*-2-*methyl*-1-*butanone* (**4e**, R′ = PhCD$_2$)

This compound was prepared from the condensation of 0.42 g (0.0010 mol) of 1-phenyl-1-propenyloxytributyltin with 0.12 g (0.0010 mol) of 1,1-dideuterophenylacetaldehyde at +45°. The crude product was analyzed by reverse-phase HPLC (acetonitrile-water: 35–65, 2.0 mL/min), Retention time 16.02 (e), 18.55 (t). The residue was purified by radial chromatography (silica gel, 15% ethyl acetate-hexane) to yield 0.18 g (70%) of the *erythro* isomer. The product was recrystallized from ether, m.p. 105–106°; IR (nujol) 3350–3200 cm^{-1} (OH), 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.25–1.31 (d, 3H, J = 7.30 Hz, C–CH$_3$), 2.97–3.45 (m, 1H, CH–CO), 4.16–4.33 (d, 1H, J = 3.71 Hz, CH–O), 7.17–8.02 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.31, 40.5, 43.3, 72.60, 126.22, 128.20, 128.40, 129.00, 129.80, 133.15, 135.60, 138.00, 204.00 (C=O).

4,4-*Dideutero*-1,4-*diphenyl*-3-*hydroxy*-2-*methyl*-1-*butanone*, (**4t**, R′ = PhCD$_2$)

This compound was obtained by the condensation of 0.42 g (0.0010 mol) of 1-phenyl-1-propenyloxytributyltin with 0.12 g (0.0010 mol) of 1,1-dideutero- phenylacetaldehyde at −78°, according to the general procedure. The crude product was analyzed by reverse-phase HPLC (acetonitrile–water: 35–65, 2 mL/min). Retention time 16.02 (e), 18.55 (t). The residue was purified by radial chromatography (silica gel, 15% ethyl acetate-hexane) to yield 0.17 g (67%) of the product as a white solid which was crystallized from hexane, m.p. 80–81° (same as for undeuterated product **4t**, R′ = PhCH$_2$); IR (nujol) 3400–3200 cm^{-1} (OH), 2580 cm^{-1} (C–D), 1675 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.23–1.30 (d, 3H, J = 7.08 Hz, –C–CH$_3$), 3.48–3.62 (m, 1H, –CH–CO–), 4.01–4.06 (d, 1H, J = 5.61 Hz, CH–CD$_2$), 7.08–7.93 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.27, 42.00, 44.30, 74.96, 126.16, 128.15, 128.44, 129.08, 133.11, 136.32, 138.07, 205.09 (C=O).

3-Hydroxy-2-methyl-1-phenyl-1-hexanone (**4**, R′ = Pr)

Condensation of 0.42 g (0.0010 mol) of 1-phenyl-1-propenyloxytributyltin with 0.072 g (0.0010 mol) of butyraldehyde at −78°, according to the general procedure afforded the product. The crude product mixture was analyzed by reverse-phase HPLC (acetonitrile-water: 35–65, 1.5 mL/min). Retention time 12.82 (e), 14.35 (t). The crude mixture was purified by radial chromatography (silica gel, 15% EtOAc–hexane) to yield 0.14 g (70%) of the product as a pale yellow viscous liquid, IR (neat) 3400–3200 cm^{-1} (OH), 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.91–1.14 (m, 5H), 1.21–1.28 (d, 3H, J = 7.08 Hz, $-CCH_3-CO-$), 1.31–1.58 (m, 2H), 3.26–3.90 (m, 1H, $-CH-CO-$), 7.28–8.11 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.00, 15.34, 18.96, 36.95, 45.76, 73.61, 128.16, 128.44, 133.05, 136.55, 209.24 (C=O). Calc for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79%. (Found: C, 75.58; H, 9.15).

Condensation of benzaldehyde with 1-cyclohexenyloxytriphenyltin generated in situ[12]

To a soln of 0.3 mL (0.002 mol) of diisopropylamine, 5 mL of dry THF and a few crystals of bipyridine (as an indicator for excess lithium diisopropylamide) at −30° under N_2 was added 1.5 mL (1.6 M, 0.002 mol) of n-BuLi slowly, with stirring. Then 0.2 g (0.002 mol) of cyclohexanone was added, the soln was cooled to −78°, and 0.72 g (0.0020 mol) of triphenyltin chloride in 5 mL of dry THF was added dropwise. The resulting mixture was allowed to stir for 30 min and then 0.2 g (0.002 mol) of benzaldehyde was added dropwise. The mixture was then stirred for 90 min at −78° and was quenched with a MeOH–water mixture, washed successively with dilute HCl, $NaHCO_3$ and brine soln. The organic layer was dried over $MgSO_4$, filtered, the solvent was removed on a rotary evaporator, and the residue was analyzed for the *erythro* to *threo* of 2-(hydroxyphenylmethyl)cyclohexanone by ^1H NMR. ^1H NMR ($CDCl_3$) δ 1.2–2.2 (m, 9H), 4.8 (d, J = 9.0 Hz), 5.3 (d, J = 3.0 Hz), 7.1–7.3 (s, 5H). The ratio of the signals at δ 4.8 (for *threo* isomer) and 5.3 (for *erythro* isomer) was 66:34.

Procedure for the reaction of cyanomethyltributyltin with nitrobenzaldehydes

To a soln of 0.045 g (0.066 mol) of benzylchlorobis(triphenylphosphine)palladium(II) and 0.15 g (0.0010 mol) of *o*-nitrobenzaldehyde in 2 mL of dry hexamethylphosphoramide (HMPA) at ambient temp was added 0.66 g (0.0020 mol) of cyanomethyltributyltin reagent. The resulting mixture was allowed to react for 24 h at ambient temp, was quenched with water, and the product was extracted with ether. The solvent, HMPA, was removed by washing the ether extract several times with water. The organic layer was then dried over $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The pure product was obtained by radial chromatography (silica gel, 20% EtOAc–hexane).

The Pd(II) complexes containing chiral ligands were prepared by stirring a mixture of the equimolar amounts of bis(benzonitrile)dichloropalladium(II) and the chiral phosphine ligands, for 30 min prior to the addition of any starting materials and then the reaction was carried out as above.

2-Hydroxy-2(o-nitrophenyl)propionitrile (**7a**)

From the condensation of 0.15 g (0.0010 mol) of *o*-nitrobenzaldehyde with 0.66 g (0.0020 mol) of cyanomethyltributyltin according to the general procedure, 0.21 g (70%) of the product was collected as a yellow solid. The product was crystallized from hexane–ether mixture, m.p. 81–83.5°; IR (nujol) 2230 cm^{-1} (C ≡ N); ^1H NMR ($CDCl_3$) δ 2.91–3.05 (dd, 2H, $-CH_2-$), 5.62 (br m, 1H, $-CH-CH_2$), 7.44–8.08 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 27.49, 65.38, 116.76 (C ≡ N), 124.76, 128.14, 129.37, 134.22, 136.67. Calc for $C_9H_8N_2O_3$: C, 56.26; H, 4.19%. (Found: C, 56.25; H, 4.24).

2-(o-Nitrophenyl)propionitrile (−)-α-methoxy-α-trifluoromethylphenylacetate

A mixture of 0.1 g (0.5 mmol) of 2-hydroxy-2-(*o*-nitrophenyl)propionitrile, 0.14 g (0.55 mmol) of (−)-α-methoxy-α-trifluoromethylphenylacetyl chloride[19] and a few drops of pyridine in 5 mL of CCl_4 was allowed to react for 12 h at ambient temp. The mixture was quenched with 2 ml of 1N HCl and the product was extracted with ether. The ether layer was washed with $NaHCO_3$ aq, water and brine soln and was dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was analyzed by reverse-phase HPLC (acetonitrile–water: 48–52, 1.5 mL/min). Retention times were 16.62 and 17.95 for the two diastereomers. Purification was done by radial chromatography (silica gel, 20% EtOAc–hexane) to yield 0.35 g (75%) of the product as a mixture of the two diastereomers. The product was crystallized from ether, m.p. 95–96°; IR (nujol) 2230 cm^{-1} (C ≡ N), 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.08–3.20 (dd, 2H, $-CH_2-$), 3.45–3.66 (2s, 3H, $-OCH_3$), 6.62–6.80 (m, 1H, $-CH-C-$), 7.20–8.16 (m, 9H, Ar); ^{13}C NMR ($CDCl_3$) δ 24.74, 55.46, 56.10, 68.24 ($-OCH_3$ of one diastereomer), 68.59 ($-OCH_3$ of the other diastereomer), 78.23, 84.94, 115.3, 124.99, 126.92, 127.38, 128.55, 129.78, 130.07, 130.19, 131.07, 131.71, 131.82, 134.16, 134.28, 147.00, 164.87 (C=O). Calc for $C_{19}H_{15}F_3N_2O_5$: C, 55.58; H, 3.70%. (Found: C, 55.58; H, 3.72).

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