ketone. This was further purified by high-pressure liquid chromatography on silica gel (Waters Prep 500, elution with petroleum ether–ethyl acetate, 95:5): IR (neat, cm^{-1}) 3620, 3440, 2955, 2905, 2875, 1642, 1455, 1425, 1387, 1319, 1040, 922; ^1H NMR ($CDCl_3$) δ 5.37 (br s, 1 H), 4.06 (br s, 1 H), 2.48–2.17 (m, 4 H), 2.17–1.9 (m, 1 H), 1.88 (s, 3 H), 1.48 (s, 1 H), 1.3–1.14 (m, 1 H), 1.27 (s, 3 H), 1.08 (s, 3 H); *m/e* (M^+) calcd 166.1358, obsd 166.1352; $[\alpha]^{27}_D$ −30.9, $[\alpha]^{27}_{365}$ −3.0° (*c* 1.45, EtOH).

The enantiomeric purity of **24** was determined as follows. The alcohol (23.3 mg, 0.14 mmol) was treated in the same manner as **19**. After chromatography of most of the sample, 45 mg of ester was obtained. ^{19}F NMR ($CDCl_3$, δ relative to α,α,α-trifluorotoluene) 8.55 (major diastereomer, 94.7%), 7.83 (minor diastereomer, 5.3%), or 89% ee; this value was corroborated by integration of ^1H NMR (in $CDCl_3$) signals of δ 3.60 and 3.48, respectively.

(+)-(1*S*)-3,7,7-Trimethylbicyclo[4.1.1]octa-2,4-diene (9). A. Dehydration of 24. A solution of 24 (48 mg, 0.30 mmol) in triethylamine (4 mL) and dichloromethane (2 mL) was treated at −20 °C with methanesulfonyl chloride (163 μL, 2.1 mmol). The mixture was stirred for 0.5 h and warmed to room temperature for an additional 0.5 h. Two such runs were quenched with water, combined, and diluted with pentane. The organic layer was washed with 10% potassium bisulfate solution and water, dried, concentrated, and filtered through Florisil with pentane. Preparative VPC (12 ft × 0.25 in. 15% SE-30 on Chromosorb G, 145 °C) gave 4.3 mg of **9**: ^1H NMR ($CDCl_3$) δ 6.09–5.95 (m, 1 H), 5.84–5.71 (m, 2 H), 2.59–2.33 (m, 3 H), 1.85 (d, J = 1.5 Hz, 3 H), 1.25 (s, 3 H), 1.17–1.05 (m, 1 H), 0.78 (s, 3 H); λ_{max} (C_2H_5OH) 305 (ϵ 1010), 294 (2220), 283 (2490); $[\alpha]^{25}_D$ +0.7, $[\alpha]^{25}_{365}$ +78.5° (*c* 0.145, $CHCl_3$).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.12; H, 10.84.

B. Shapiro Reaction on 22. A solution of **22** (2.0 g, 12.2 mmol) and (*p*-toluenesulfonyl)hydrazine (2.72 g, 14.6 mmol) in methanol (15 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by high-pressure liquid chromatography (elution with petroleum ether–ethyl acetate, 85:15) to give the tosylhydrazone (2.62 g, 65%) as a colorless crystalline solid, mp 162–165 °C dec (from petroleum ether–ethyl acetate).

A 1.5-g (4.5 mmol) sample of the tosylhydrazone was added to a solution of diisopropylamine (40 mL, 29 mmol), *n*-butyllithium (18 mL of a 1.5 M solution, 27 mmol), and hexamethylphosphoramide (4.8 mL, 29 mmol) in the manner described above. Following chromatography on alumina, **9** was obtained as a colorless oil (350 mg, 52%), identical in all respects with the hydrocarbon obtained in A.

Acknowledgment. Partial financial support for this research was provided by the National Science Foundation (Grant CHE 79-00333) to whom we are grateful. Dr. A. W. Potts of the Physics Department, King's College, London, is thanked for the UV photoelectron spectrum of diene **8**.

Registry No. (1*S*)-**4**, 62235-10-3; (1*S*)-**6**, 86689-39-6; (1*R*)-**7**, 86689-40-9; (1*S*)-**8**, 86689-41-0; (1*S*)-**9**, 86689-42-1; (1*R*)-**10**, 72453-33-9; (1*R*)-**11**, 86689-43-2; (1*R*)-**12**, 86689-44-3; **13a**, 86689-45-4; **13b**, 86689-46-5; (1*R*)-**13b** (−)-α-methoxy-α-(trifluoromethyl)phenylacetate (isomer 1), 86689-47-6; (1*R*)-**13b** (−)-α-methoxy-α-(trifluoromethyl)-phenylacetate (isomer 2), 86709-31-1; **14a**, 86689-48-7; **14b**, 86689-49-8; (1*R*)-**16**, 34153-03-2; (1*R*)-**17**, 86709-32-2; (1*R*)-**18**, 86689-50-1; (1*R*)-**19**, 86689-51-2; (1*R*)-**20**, 86689-52-3; (1*R*)-(*E*)-**21**, 86689-53-4; (1*R*)-(*Z*)-**21**, 86709-33-3; (1*R*)-**22**, 86689-54-5; (1*R*)-**22** tosylhydrazone, 86695-74-1; (1*R*)-(*E*)-**23**, 72453-37-3; (1*R*)-**24**, 86689-55-6; (1*R*)-**24** (−)-α-methoxy-α-(trifluoromethyl)phenylacetate (isomer 1), 86689-56-7; (1*R*)-**24** (−)-α-methoxy-α-(trifluoromethyl)phenylate (isomer 2), 86709-34-4; (+)-nopinone, 38651-65-9; (−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 39637-99-5.

Mechanisms of the Palladium-Catalyzed Couplings of Acid Chlorides with Organotin Reagents

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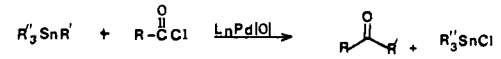
Abstract: In the coupling reaction of benzoyl chloride with phenyltributyltin catalyzed by the introduction of benzylchlorobis(triphenylphosphine)palladium(II) (**1**), the disappearance of **1** was observed in the ^{31}P spectrum of the reaction mixture with the appearance of benzoylchlorobis(triphenylphosphine)palladium(II) (**3**); benzophenone was obtained as a product of the reaction. The reaction of **3** with phenyltributyltin also yields benzophenone and is retarded by added triphenylphosphine. The results are consistent with a catalytic cycle involving sequential fast oxidative addition of benzoyl chloride to a palladium(0) complex (generated from **1**) to give **3**, slow transmetalation of **3** with the tin reagent, and fast reductive elimination to regenerate the palladium(0) complex. The rates of the transmetalation reaction of unsymmetrical organotrimethyltin or organotributyltin ($R'SnR_3$) with **3** in the catalytic reaction followed the order R′ = PhC≡C > PrC≡C > PhCH=CH, CH_2=CH > Ph > $PhCH_2$ > CH_3OCH_2 > CH_3 > Bu. The transfer of benzyl groups, R′, from tin to **3** is accelerated to some extent by +σ substituents in polar solvents, showing a slightly positive ρ, 1.2. Vinyltin reagents appear to undergo transmetalation with **3** (catalytic reaction) predominately with retention of geometry at the double bond. Inversion of configuration at carbon takes place at an sp^3 carbon (R′) bound to tin when the transmetalation reaction of **3** is carried out in a polar solvent. These results are consistent with a transmetalation reaction in which electrophilic cleavage of the carbon–tin bond takes place, with palladium(II) (**3**) acting as the electrophile.

The palladium-catalyzed coupling reaction of acid chlorides with organotin reagents has been demonstrated to be an efficient reaction that gives ketones in high yields.[1,2] The reaction is quite general with respect to both coupling partners and can be carried out in a number of solvents, including HMPA, chloroform, dichloroethane, and THF. The ketone product is formed rapidly under mild, neutral reaction conditions, and catalytic turnovers of 1000 have been achieved. There is no further addition to the product ketone, and a wide variety of functional groups can be tolerated on the acid chloride, including nitro, nitrile, haloaryl, methoxy, ester, and even aldehyde.[1]



The tetraorganotin reagents transfer the first group rapidly, but the second leaves about 100 times slower from R_3SnCl. More recently, this reaction has been carried out with acetylenic tin

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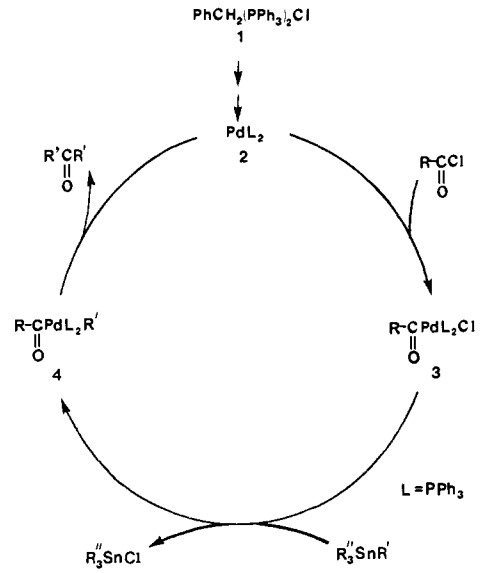

Figure 1. Catalytic cycle for the coupling reaction of acid chlorides with tetraorganotins.

reagents to yield acetylenic ketones[3] and has been used for the synthesis of a key methyl ketone intermediate in the total synthesis of (±)-quadrone.[4]

In the proposed[1] catalytic cycle for this reaction (Figure 1) the active catalyst bis(triphenylphosphine)palladium(0) (**2**)—generated from benzylchlorobis(triphenylphosphine)palladium(II) (**1**)—undergoes oxidative addition of the acid chloride to give the acylchloropalladium complex **3**. A transmetalation reaction between **3** and the organotin yields an acylalkylpalladium(II) species (**4**), which undergoes reductive elimination of the ketone and regenerates **2**.

Although the mechanisms of the oxidative addition[5,6] and 1,1-reductive elimination reactions[6-8] of palladium have received considerable attention, to the extent that they are reasonably well understood, most transmetalation reactions have been given scant attention, and consequently our comprehension of the mechanisms is limited.

The transmetalation reaction **3** → **4**, in the palladium-catalyzed ketone synthesis, has been proposed to occur by the electrophilic attack of the acylchloropalladium(II) complex on the carbon bonded to tin.[1] A similar proposal has been offered for the transmetalation reactions between organotin reagents and platinum(II) complexes.[9,10] These suggestions are based on a knowledge of the reactivity of organotins with standard electrophiles;[11-14] nevertheless, there is little direct evidence to support the electrophilic cleavage mechanism.

Results and Discussion

The acylalkylpalladium(II) product of the transmetalation reaction **3** → **4** (Figure 1) has not been isolated, presumably because the reductive elimination reaction is faster than transmetalation. Organotin reagents undergo two types of reactions with platinum complexes; transmetalation takes place with platinum(II) halides[15] while oxidative addition takes place with platinum(0) complexes.[16] In the palladium-catalyzed coupling of unsymmetrical organotins with acid chlorides, the groups of tin that react selectively—in preference to methyl or butyl groups—have a site of unsaturation at a carbon that is either directly bonded to tin or one carbon removed from tin[1] (vide infra). This selectivity is analogous to the transmetalation reactions between organotins and platinum.[9,10,15,17]

This same selectivity also has been observed in the oxidative addition reactions of organotins to platinum(0) complexes. Although the product of oxidative addition of the carbon–tin bond of an organotin reagent has not been observed with a palladium(0) complex, the following also is a plausible sequence of events in the catalytic coupling reactions of organotins with acid chlorides.

$$L_nPd(0) + R'SnR''_3 \longrightarrow L_2Pd(R')SnR_3 \xrightarrow{RCOCl} L_2Pd(RCO)(R') + R''_3SnCl$$

The Catalytic Cycle. Support for a catalytic cycle (Figure 1) in which transmetalation of the acylpalladium chloride by the organotin reagents, **3** → **4**, takes place and direct proof that the acylpalladium chloride complex **3** is present in the catalytic cycle were obtained as follows: The reaction of benzoyl chloride (R = C_6H_5) and phenyltributyltin (R′ = C_6H_5, R″ = *n*-Bu), catalyzed by 17 mol % of benzylchlorobis(triphenylphosphine)palladium(II) (**1**), could be followed by ^{31}P NMR.

$$Bu_3SnPh + PhC(=O)Cl \xrightarrow[65^\circ C, CDCl_3]{17\ mole\%\ 1} PhC(=O)Ph + Bu_3SnCl$$

2 : 1

Disappearance of the peak characteristic of **1** (28.7 ppm) and the concomitant appearance of a single peak at 19.6 ppm was observed with time. The peak at 19.6 ppm was identical with that observed for an independently prepared sample of benzoylchlorobis(triphenylphosphine)palladium(II) (**3**, R = Ph).[18] Minor amounts of other peaks not identified possibly are from the complexes formed in the conversion of **1** to bis(triphenylphosphine)palladium(0) (**2**).[1] After a 15-min reaction, **3** was the predominate species, and after 90 min, a 76% yield of benzophenone was obtained.

The presence of **3** as the predominate species in the catalytic reaction suggests that the transmetalation step **3** → **4** is rate determining and all other steps—reductive elimination and oxidative addition—are fast. The oxidative addition reaction of benzoyl chloride to tetrakis(triphenylphosphine)palladium(0) in THF at −30 °C has a half-life of 10 min;[19] therefore the oxidative addition to **2** at 65 °C must be fast. Also, a fast reductive elimination step relative to transmetalation is consistent with the observation that tetrabutyltin gives a high yield of butyl ketones, both in chloroform and HMPA without β-hydride elimination occurring.[1,20]

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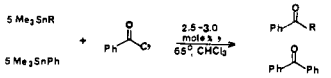
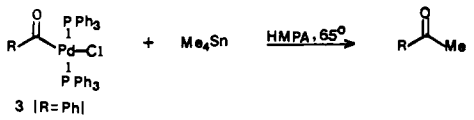
Table I. Relative Reaction Rates of Benzoyl Chloride with Organotins Catlayzed by **1**



R'	Solvent	– R –								
		PhC≡C–	*n*-PrC≡C–	PhCH=CH–	CH_2=CH–	Ph–	$PhCH_2$–	CH_3OCH_2–	CH_3–	*n*-Bu–
Me	$CHCl_3$	46	2?	>0	8	?	–	0.5	0.?	–
Bu	$CHCl_3$	>00	48	>0	>7	1	–	–	–	0.0?
Bu	HMPA	–	>>00	–	70	?	0.5	–	–	0.?4

When tetramethyltin was allowed to react with **3** (R = Ph), or with benzoyl chloride in the presence of **1**, acetophenone was produced in high yields. When these reactions were carried out



3 (R=Ph)

in the presence of added triphenylphosphine, the rate of the reaction was retarded. Thus, it is possible that phosphine inhibits the transmetalation reaction, and a free coordination site on palladium is necessary for transmetalation to occur. However, phosphine also inhibits reductive elimination from dialkyl palladium(II) complexes.[7]

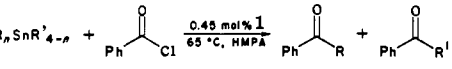
When the coupling reaction was conducted with an equivalent each of benzoyl chloride, tetramethyltin, and methyltriphenyltin in the presence of 0.7 mol % of **1** in $CDCl_3$ at 65 °C no phenyltrimethyltin or dimethyldiphenyltin were observed (^{1}H NMR). Similarly, when both methyltriphenyltin and phenyltrimethyltin were present in the reaction mixture, no dimethyldiphenyltin was observed. Scrambling does occur in the redistribution of two organotin reagents in the presence of aluminum chloride.[13] The lack of scrambling in the reactions catalyzed by palladium indicates that either the transmetalation process is irreversible or the acylalkylpalladium complex (**4**) undergoes reductive elimination at a faster rate than the reverse transmetalation.

Transfer Order. The determination of the transfer order of different organic groups from tin in the palladium-catalyzed coupling with acid chloride gives information as to how readily different groups undergo the transmetalation reaction. Where a group is selectively transferred from an organotrialkyltin (unsymmetrical tin reagent), a competitive reaction was used to determine their relative reactivity. Competitive tin reagents were selected such that the trialkyltin chloride product would be the same for each reagent. The coupling reaction of benzoyl chloride was carried out in the presence of 5 equiv each of two unsymmetrical organotin reagents in the presence of **1** as the catalyst, and the reaction mixture was analyzed for the two product ketones. Since the transmetalation reaction very likely is the rate determining step and is probably irreversible, the ratio of products should be a good approximation of the relative rate of transmetalation. The ketone products were stable under the reaction conditions, and their relative ratios were determined by HPLC (Table I). The reaction carried out in chloroform by competition of organotrimethyltin vs. phenyltrimethyltin or by competition of organotributyltin with phenyltributyltin gave the same transfer order—with the exception of the reversal of the order of styryl and vinyl. In a more polar solvent, HMPA, the relative transfer rate of acetylenic and vinyl groups is greatly accelerated. This same transfer order is that observed for transmetalation reactions of organotins and platinum(II) complexes,[15] and the electrophilic cleavage of organotrimethyltin compounds by mercuric chloride also shows the same order of reaction: PhC≡C (very fast) > CH_2=CH (**5**) > Ph (**1**) > Me (0.007).[21] These results are consistent with an electrophilic cleavage reaction in the transmetalation step in which the acylpalladium chloride complex (**3**) is the electrophile that attacks the carbon attached to tin. The transfer order also is consistent with a transition state in which considerable charge is developing at carbon of the migrating group.

In an effort to assess the relative transfer order of different alkyl groups, unsymmetrical organotins and benzoyl chloride were allowed to react in HMPA in the presence of catalyst I (Table II). The order Me > Bu, Et > *i*-Pr, was consistent with electrophilic cleavage reactions of tetraalkyltins in polar solvents.[22] Quantitatively, there is a difference in the transfer order depending on the identity of R″; these groups that do not transfer affect the rate of transfer of the R′ group.

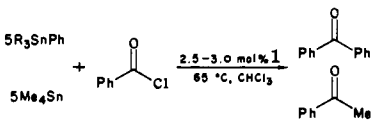
In chloroform, phenyltrimethyltin was 10 times more reactive than tetraphenyltin in the transfer of a phenyl group. From the relative transfer order (Table I), it might be expected that from trimethylphenyltin, a 10:3 mixture of benzophenone to acetophenone would be obtained, yet there is virtually no transfer of a methyl group using this reagent. When three competitive coupling reactions were conducted between 5 equiv of tetramethyltin and phenyltrimethyltin, phenyltributyltin, or triphenylmethyltin, the ratios of benzophenone to acetophenone were determined (Table III). This ratio, measuring the reactivity of each phenyltin relative to tetramethyltin, showed that phenyltrimethyltin and phenyltributyltin had approximately the same reactivity. However, the reactivity of triphenylmethyltin was 6 times less than the phenyltrimethyltin or phenyltributyltin reagents.

Table II. Palladium-Catalyzed Reaction of Unsymmetrical Tetraalkyltins with Acid Chlorides



n	R	R′	PhC(=O)R/ PhC(=O)R′
3	Me	Et	83:17
2	Bu	*i*-Pr	100:0
2	Me	Bu	57:43

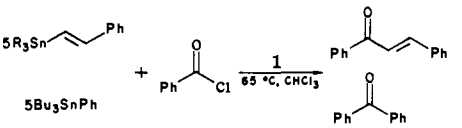
Table III. Reactivity of Phenyltin Compounds Relative to Tetramethyltin



R_3	PhC(=O)Ph/ PhC(=O)Me[a]
Me_3	17
Bu_3	15
Ph_2(Me)	2.5

[a] Product ratio determined by HPLC.

Table IV. Reactivity of Styryltins Relative to Phenyltributyltin



R_3	PhC(=O)C=CPh/ PhC(=O)Ph[a]
Me_3	10
Bu_3	10
Ph_3	0.3

[a] Product ratio determined by HPLC.

(20) If transmetalation takes place to give the *trans*-acylbutyl complex; then both trans to cis isomerization and reductive elimination must take much faster than β-elimination. If the *cis*-acylbutyl complex is generated directly, the 1,1-reductive elimination has been shown to take place to yield ketone with the exclusion of β-elimination. Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1981**, 289.

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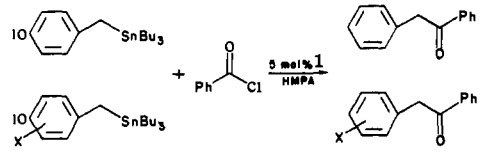
Table V. Reactivity of Substituted Benzyltributyltins Relative to Benzyltributyltin and Their Hammett Substituent Values



X	$\frac{P(X)}{P(H)}$	$\log\frac{P(X)}{P(H)}$	σ	σ^+
3-NO_2	3.0	0.48	0.710	0.78
3-CF_3	4.4	0.64	0.430	0.52
3-F	2.5	0.39	0.337	0.31
H	1	0	0	0
3-Me	0.82	−0.086	−0.07	−0.07
4-Me	0.72	−0.14	−0.17	−0.31
4-MeO	0.60	−0.22	−0.27	−0.78
4-PhO	0.44	−0.35	−0.32	−0.90

Thus, the replacement of more than one methyl or butyl group on the organotin reagent by phenyl slows down the rate of a single phenyl transfer.

An analogous series of competitive coupling reactions was conducted between phenyltributyltin and trimethyl-, tributyl-, or triphenylstyryltin (Table IV). Both trimethyl- and tributylstyryltin were 10 times more reactive than tributylphenyltin. By contrast, triphenylstyryltin was only a third as reactive as tributylphenyltin.[23]

The lower reactivity of organotin reagents containing more than one phenyl group attached to tin could be a consequence of the electron-withdrawing effect of the phenyl groups and is again consistent with electrophilic cleavage at the carbon–tin bond by attack of the electrophile on the carbon attached to tin. This same effect has been observed in the protonic acid cleavage of phenyl,[24] allyl,[25] and vinyl[26] groups attached to tin. The presence of phenyl or vinyl groups on the leaving tin group deactivates the organotin as a result of the decreased ability of the groups to support a positive charge on tin in the transition state.

The relative transfer order in tetraorganotin reagents synthetically is a fortunate consequence. Because in practice only one group is transferred from tin, if the partner to be transferred is a difficultly synthesized or expensive group, then the utilization of only one of the four of these partners would be a distinct disadvantage. Because there is selectivity in group transfer, an unsymmetrical organotin reagent containing three alkyl anchoring groups can be utilized to transfer the more elaborate group.

Linear Free Energy Relationship for Transmetalation. In order to ascertain the electronic effects in transmetalation, the rates of reaction of substituted benzyltin reagents relative to unsubstituted benzyltins were correlated with the Hammett substituent constants, σ. The determination of the relative rates (rate ratios) were obtained by conducting competitive catalytic coupling reactions between the two benzyltin reagents and obtaining the product ratios rather than the ratios of rate constants. Because our evidence supports a transmetalation reaction that is irreversible and rate determining, the product ratios could be used in place of the ratios of rate constants. A 10-fold excess of each tin reagent was utilized in a competitive reaction, along with 5 mol % of **1**. High yields of ketones in the coupling reactions of the benzyltin reagents with benzoyl chloride (1:1 molar ratio) in the presence of 4 mol % of **1** were obtained in all cases, except in that reaction with (3-nitrobenzyl)tributyltin, in which a moderate yield was realized.

(23) The transfer of phenyl groups from triphenylstyryltin occurs to an extent that was corrected for by running coupling reactions with triphenylstyryltin alone.

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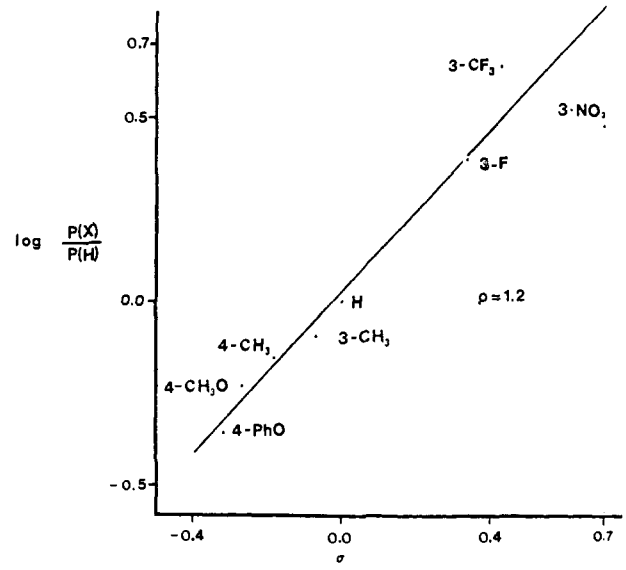
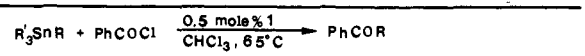


Figure 2. Plot of log $(P(X)/P(H))$ vs. σ.

Table VI. Stereochemistry of Alkenyl Group Transfer in the Palladium-Catalyzed Coupling of Acid Chlorides with Organotins



R'_3SnR	E/Z	PhCOR	E/Z
$Me_3Sn-CH=CHPh$	95/5	Ph−CO−CH=CHPh	100/0
	15/85		100/0
	15/85		33/66[a]
$Bu_3Sn-C(CH_3)=CH-CH_3$	25/75	$Ph-CO-C(CH_3)=CH-CH_3$	30/70
$Bu_3Sn-CH=CH-CH_2OR''$[b]	85/15	$Ph-CO-CH=CH-CH_2OR''$[b]	84/16

[a] The reaction was run in the dark in the presence of 2,6-di-*tert*-butylphenol. [b] R'' = Si(*t*-Bu)Me_2.

The results (Table V, Figure 2) gave the best correlation when log $(P(X)/P(H))$ was plotted vs. normal σ-substituent constants. There was considerable deviation for the 3-NO_2 substituted benzyltin reagent. Excluding this point, a least-squares treatment gave a ρ of 1.2, a Y intercept of 0.043, and a correlation coefficient of 0.987. The deviation observed for the 3-NO_2 point possibly could be a result of the instability of the ketone product, 3-nitrodeoxybenzoin, under the reaction conditions, since the ketone was the only derivative of deoxybenzoin found to be unstable to chromatography on silica gel, although an HPLC analysis was carried out on a reverse-phase column.

Transmetalation was accelerated slightly by electron-withdrawing groups, and the better correlation with σ rather than σ^+ indicates little conjugation between the benzyl carbon and the phenyl ring (and its substituent) in the transition state. The slightly positive ρ also suggests that carbon–tin bond breaking precedes palladium–carbon bond making in the transition state.

Stereochemistry of Transmetalation. The stereochemistry of the transmetalation reaction with respect to the vinyl group transfer from tin was carried out utilizing either pure or known mixtures of geometric isomers of different vinyltrialkyltins. The geometry of the double bond in the tin reagent was compared to the geometry of the α,β-unsaturated ketone product. Since the 1,1-reductive elimination of an alkenyl group and a methyl group attached to palladium takes place with retention of geometry at the sp^2 carbon,[7e] the stereochemistry of the transmetalation could be determined.

Although the reaction of (*E*)-styryltrimethyltin gave (*E*)-chalcone in a reaction with benzoyl chloride catalyzed by **1** (Table VI), the reaction of (*Z*)-styryltrimethyltin (*E*/*Z*, 15/85) also gave (*E*)-chalcone. (*Z*)-Chalcone (*E*/*Z*, 20/80) was not isomerized under the reaction conditions, but the isomerization of the tin

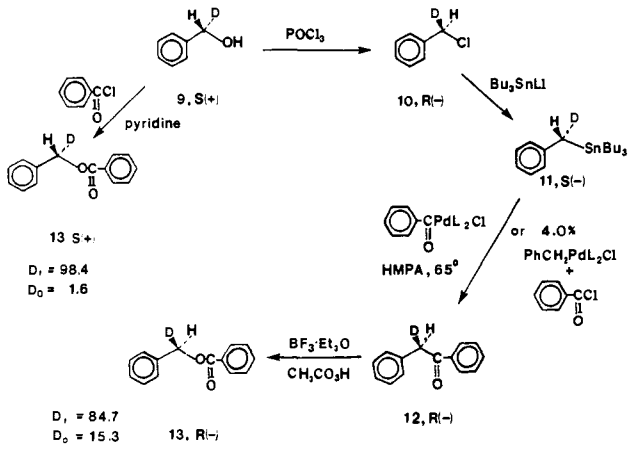
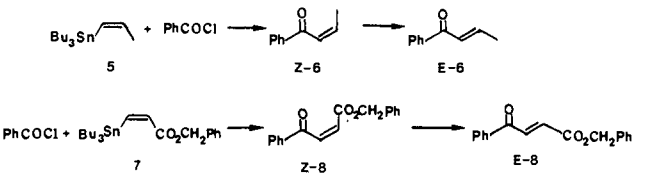


Figure 3. Stereochemical sequence in the determination of the stereochemistry of transmetalation.

reagent (*Z*)-styryltrimethyltin takes place under radical conditions. Addition of 10% 2,6-di-*tert*-butylphenol to the coupling reaction of a 15/85 mixture of (*E*)- to (*Z*)-styryltrimethyltin gave a 34/66 mixture of (*E*)- to (*Z*)-chalcone. Reaction of a 25/75 mixture of (*E*)- and (*Z*)-2-buten-2-yltributyltin gave a 30/70 mixture of (*E*)- to (*Z*)-1-phenyl-2-methyl-2-buten-1-one and reaction of an 85/15 mixture of (*E*)- and (*Z*)-3-(*tert*-butyldimethylsiloxy)-1-propenyltributyltin gave an 84/16 mixture of *E*/*Z* ketone.

Although the reaction of (*Z*)-1-propenyltributyltin (**5**) gave a 50/50 mixture of (*E*)- to (*Z*)-1-phenyl-2-buten-1-one (**6**) the product was shown to isomerize under the reaction conditions, so that this reaction could not be used to determine the stereochemistry of the transmetalation. Similarly, in a coupling reaction of (*Z*)-benzyl 3-(tributylstannyl)propenoate (**7**), either the *E* ketone **8** ($CHCl_3$ solvent) or predominately *E* mixture (*E*/*Z*, 62/38, THF solvent) was obtained, but again the product α,β-unsaturated ketone was isomerized under the reaction conditions.



Thus, retention of geometry at carbon predominates in the coupling reactions of vinyltin reagents, and this requires retention of geometry in the transmetalation. Retention of the double bond also has been observed in the cleavage reactions of alkenyltins with electrophiles.[26]

From a synthetic standpoint the isomerization of alkenylketones imposes a limitation, but isomerization of such α,β-unsaturated ketones occurs quite readily. However, if the (*E*)-alkenyl ketone is desired, this reaction can be advantageous, since *Z* or *E*/*Z* mixtures of the organotin reagent can be used.

Since the 1,1-reductive elimination of two organic partners from a diorganopalladium(II) complex is known[8a] to take place with retention of configuration at the carbon bound to palladium, the only step of unknown stereochemical consequence in the catalytic cycle—in the case of an sp^3 carbon bound to tin—is the transmetalation reaction (Figure 1). Thus, by conducting a catalytic reaction with benzoyl chloride and (*S*)-(−)-(α-deuteriobenzyl)-tributyltin (**11**) in the presence of **1** and observing the absolute configuration of the (α-deuteriobenzyl)phenyl ketone product, **12**, the stereochemistry of the transmetalation process could be unambiguously defined (Figure 3).[27]

(*S*)-(+)-Benzyl-α-*d* alcohol (**9**),[28a] 84.2% ee, was treated with $POCl_3$ in pyridine/CH_2Cl_2 to give (*R*)-(−)-benzyl-α-*d* chloride (**10**), 75.0% ee.[28b] Tributyltin hydride was converted to lithium tributylstannate[29] and added to a THF solution of **10** at 0 °C to yield (*S*)-(−)-(α-deuteriobenzyl)tributyltin (**11**).[30] The absolute configuration of **11** was not directly determined. Although there is controversy concerning the degree of nucleophilic substitution vs. an electron-transfer pathway in this reaction,[30-33] the net inversion of configuration is high, often greater than 90%.[30,33,34]

The reaction of 1.03 equiv of **11** with 1.00 equiv of benzoyl chloride and 4.0 mol % **1** in HMPA was carried out at 65 °C for 16 h to yield 71% of (−)-**12**, $[\alpha]^{20}_D$ 0.314° (CCl_4, *c* 30.3). Alternatively, the reaction of benzoylchlorobis(triphenylphosphine)palladium(II) (**3**, R = Ph) with 1.04 equiv of **11** in HMPA at 65 °C for 1.5 h also afforded (−)-**12**.

In order to determine the absolute configuration of **12**, a Baeyer–Villiger oxidation of **12** was carried out with a mixture of boron trifluoride etherate and 40% peracetic acid in chloroform at 45 °C for 30 h[35] to yield (−)-α-deuteriobenzyl benzoate ((−)-**13**), which showed $[\alpha]^{20}_D$ 0.10°; $[\alpha]^{20}_{365}$ −0.310° (CCl_4, *c* 9.0). The preparation of (*S*)-(+)-α-deuteriobenzyl benzoate ((*S*)-(+)-**13**) by the acylation of **9** with benzoyl chloride/pyridine showed $[\alpha]^{20}_D$ 0.36°, $[\alpha]^{20}_{365}$ 1.26° (CCl_4, *c* 9.0). Since the optical center of (*S*)-(+)-**9** is not affected by acylation, (*R*)-(−)-**13** (obtained from the Baeyer–Villiger oxidation) and (*S*)-(+)-**13** are enantiomers. Since the Baeyer–Villiger oxidation is known to occur with retention of configuration at the saturated carbon of the ketone,[36] **12** must be of the *R* configuration. Thus, the transmetalation occurs predominately with inversion of configuration at the saturated carbon being transferred.

Further characterization of **12** was provided by CD spectroscopy in the wavelength region of the n–π^* transition of the carbonyl. The CD spectrum of **12** (16.4×10^{-3} M, MeOH) gave a negative curve with $[\theta]$ = −10.3 (312 nm), while (*S*)-(+)-α-methyldeoxybenzoin (6.75×10^{-3} M) also shows a negative curve in the 312-nm region. It is known that for cyclohexanones[37] and adamantones[38] that deuterium substitution either α or β to the carbonyl group gives CD spectra that are opposite in sign to the analogous alkyl-substituted compounds of the same absolute configuration, in the wavelength region of the n–π^* transition. Correlation of (*S*)-(+)-α-methyldeoxybenzoin with **12** predicts that **12** is of the *R* absolute configuration, since both CD curves have the same sign.

The use of a chiral shift reagent, tris[3-((trifluoromethyl)-hydroxymethylene)-*d*-camphorato]europium did not provide a method of determining the enantiomeric excess of **12**. The direct determination of the optical purity of a ketone in which the optical activity is solely due to deuterium substitution has never been realized.[38] The optical purity of **13** was 21% (based on $[\alpha]^{20}$), which corresponds overall to 28% ee for the three reactions between **10** and **13**. There are points in the sequence between **10** and **13** where racemization is likely by processes other than the transmetalation step. The stereospecificity in the displacement of chloride from **10** by lithium tributylstannate could not be determined. Although this occurs with greater than 90% inversion with *S*-(+)-2-octyl chloride,[30] the displacement reaction of benzyl chloride with lithium triorganostanates is likely to be accompanied by more racemization. The reductive elimination of methyl and an α-deuteriobenzyl group from palladium(II) does not occur with complete retention of configuration at the carbon bound to palladium,[8a] such that this is another possible source of racemization.

The enolization of **12**, under acidic or basic conditions as well as deuterium loss in a protic environment would lead to loss of

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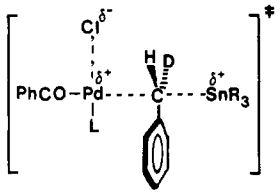
optical purity. The loss of optical activity due to deuterium loss alone can be estimated from the deuterium content (mass spectrum) D_1/D_0 **13**-*R* = 84.7:15.3; **13**-*S* = 98.4:1.6. By assuming a deuterium isotope effect of 2 for the enolization process, 42% of **12** racemized in the reactions from **11** to **13**.[39] Consequently, the highest possible optical purity that could have been realized for **12** was 43% ee, and therefore the transmetalation must have occurred with ≥65% stereospecificity.

In polar solvents such as HMPA, inversion of configuration at carbon bonded to tin in transmetalation is analogous to the stereochemistry observed in acetonitrile for the bromine cleavage of a saturated carbon bonded to tin.[40] Accordingly, the transmetalation in this catalytic reaction can be compared to an electrophilic cleavage (S_E2) in which catalytic intermediate **3** is the electrophile. The transition state for the electrophilic cleavage of a carbon–tin bond has been proposed to be either open (shown) or cyclic,[22,41,42] depending on the polarity of the solvent, the more polar solvents favoring the open transition state and inversion of configuration at carbon.



Experimental Section

Diethyl ether, tetrahydrofuran (THF), and benzene were freshly distilled under nitrogen from sodium benzophenone prior to use. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and stored over 13X molecular sieves under argon. Chloroform was passed through a short basic alumina column prior to use in the coupling reactions. Gas chromatographic analyses were carried out on a Varian Model 3700 using a 10% OV-101 Chromosorb W-80/100, 2 m × $^1/_8$ in. column and helium as a carrier gas. HPLC analyses were carried out utilizing Waters Models 6000A and M-45 pumps with a solvent programmer and a Model 440 absorbance detector. A μBondapak-C18 column was utilized for reverse-phase HPLC analyses, and a μPorasil column was utilized for normal-phase HPLC analyses. Radial chromatography was carried out with a Chromatotron (Harrison Research Co.). Flash chromatography was carried out according to the published procedure.[43] The ^{1}H NMR spectra were obtained on Varian Model EM-360 and JEOL Model FX-100 spectrometers, with tetramethylsilane as the internal standard. The ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer, with deuteriochloroform as the internal standard. The ^{31}P NMR spectra were obtained on a Nicolet NT-150 spectrometer, with 85% phosphoric acid as an external standard. Infrared spectra were obtained on a Beckman Model 4250 spectrometer. The mass spectra were obtained on a VG Micromass 16F spectrometer. The elemental analyses were performed by Micro-Tech Laboratories. High-resolution mass spectra were obtained by the Midwest Regional Center for Mass Spectrometry, Lincoln, NE.

Tin Reagent. Tin reagents either were obtained commercially or were prepared according to known methods: Phenyltrimethyltin,[44] phenyltributyl,[12] trimethylvinyltin,[45] tributylvinyltin,[45] (*Z*)-1-propenyltributyltin (**5**),[46] (*E*)-β-styryltriphenyltin,[47] (phenylethynyl)trimethyltin,[48] 1-pentynyltrimethyltin,[48] (phenylethynyl)tributyltin,[3] benzyltributyltin,[49] (4-methylbenzyl)tributyltin,[50] (4-methoxybenzyl)tributyltin,[50] ethyltrimethyltin,[51] dibutyldiisopropyltin,[52] and dibutyldimethyltin.[52]

(*E*)-β-Styryltrimethyltin. A solution of (*E*)-styryllithium was prepared in Trapp solvent from 9.35 g (0.0510 mol) of (*E*)-β-bromostyrene[53] and 45.0 mL of 2.25 M *tert*-butyllithium as described.[54] To the solution at −78 °C was added 11.5 g (0.0580 mol) of trimethyltin chloride in 50 mL of THF. The reaction mixture was maintained at −78 °C for 2 h and was then warmed to room temperature and stirred for 12 h. The clear yellow solution was quenched with 100 mL of water, and the aqueous layer was separated and washed with 100 mL of water and brine and was then dried (Na_2SO_4). The solvents were removed by distillation (1 atm) and the residue was distilled under reduced pressure to give 9.9 g (74%) of product: bp 85–90 °C (1 mmHg) [lit.[55] bp 110–114 °C (3.5 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, CH_3Sn, *Z* isomer), 0.2 (s, 9, CH_3Sn, *E* isomer), 6.7 (s, 2, =CH, E isomer), 6.9–7.4 (m, 5); ^{13}C NMR ($CDCl_3$) δ −9.42 (CH_3Sn), 125.9, 127.5, 128.3, 129.4, 138.3, 145.6. The ^{1}H NMR spectrum matched the published data.[55] The ratio of *E* to *Z* isomers was 95:5.

(*Z*)-β-Styryltrimethyltin. This compound was prepared by the same procedure as described for the *E* isomer in 52% yield: bp 56–60 °C (0.1 mmHg) [lit.[55] bp 110–114 °C (3.5 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9, CH_3Sn, *Z* isomer), 0.2 (s, CH_3Sn, *E* isomer), 6.0 (d, 1, *J* = 13.5 Hz, =CH), 6.9–7.3 (m, 5), 7.4 (d, 1, *J* = 13.5 Hz; =CH). The ratio of *E* to *Z* isomers was 15:85. The ^{1}H NMR spectrum matched the published data.[55]

(*E*)-β-Styryltributyltin. A mixture of 5.82 g (20.0 mmol) of tributyltin hydride, 1.95 g (19.0 mmol) of phenylacetylene, and 0.14 g (0.085 mmol) of azobis(isobutyronitrile) was heated slowly to 50 °C and maintained at that temperature for 24 h. The reaction mixture was cooled, a white precipitate was removed by filtration through a celite pad, and the liquid was distilled to give 6.50 g (84%) of (*E*)-β-styryltributyltin: bp 134 °C (0.1 mmHg) [lit.[12] bp 122–125 °C (0.1 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.7–1.6 (m, 27), 6.9 (s, 2, =CH), 7.2–7.4 (m, 5); ^{13}C NMR ($CDCl_3$) δ 9.74, 13.8, 27.4, 29.2, 125.9, 127.3, 128.3, 129.3, 138.7, 146.0.

(*Z*)-1-Propenyltributyltin. This compound was prepared by the reaction of propenylmagnesium bromide and tributyltin chloride following a procedure for the preparation of tributylvinyltin.[45] bp 77–78 °C (0.25 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.7–1.6 (m, 27), 1.7 (d, 3, *J* = 7 Hz, =CCH_3), 5.7 (m, 1, =CHSn), 6.4 (m, 1, =C*H*CH_3). The ^{1}H NMR Spectrum in the vinyl region matched the published data for (*Z*)-1-propenyltrimethyltin.[46]

2-Buten-2-yltributyltin. A solution of 22.3 g (0.500 mol) of 2-chloro-2-butene in 30 mL of THF was added to 12.2 g (0.500 mol) of magnesium in 75 mL of THF. The solution was heated at the reflux temperature for 5 h, cooled, treated with 48.8 g (0.150 mol) of tributyltin chloride, and stirred at ambient temperature for 10 h. The reaction was quenched with an aqueous ammonium chloride solution. The organic layer was separated and washed with 75 mL of saturated aqueous sodium bicarbonate and brine, dried (Na_2SO_4), concentrated, and distilled to give 36.0 g (70%) of product as an *E*/*Z* mixture: bp 114 °C (1.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.4–2.2 (m, 33), 5.63 (m, 1, =CH, *E* isomer), 6.10 (m, 1, =CH, *Z* isomer); ^{13}C NMR ($CDCl_3$) δ 9.16, 9.92, 13.7, 17.5, 19.8, 26.8, 27.0, 27.5, 28.0, 29.4, 134.3, 134.5, 138.4, 138.8. The ratio of *Z* to *E* was 75:25. The isomer assignment was based on comparison of the chemical shifts of the vinyl protons to the vinyl protons published for (*E*)- and (*Z*)-2-butenyltrimethyltin.[56] Anal. Calcd for $C_{16}H_{34}Sn$: C, 55.68; H, 9.93. Found: C, 55.79; H, 9.68.

Benzyl 3-(Tributylstannyl)propenoate (7). A mixture of 6.6 g (23 mmol) of tributyltin hydride, 4.0 g (25 mmol) of benzyl propiolate,[57] and 0.16 g (0.92 mmol) of azobis(isobutyronitrile) was heated slowly to 65 °C and then kept at that temperature for 15 h. The reaction mixture was purified on a 10-cm gravity column (silica gel, ethyl acetate/hexane, 10:90), followed by separation by medium-pressure LC (silica gel, ethyl acetate/hexane, 2:98) to give 6.0 g (60%) of the *Z* isomer: ^{1}H NMR ($CDCl_3$) δ 0.6–2.0 (m, 27), 5.1 (s, 2, CH_2O_2C), 6.7 (d, 1, *J* = 12 Hz, =CH), 7.15 (d, 1, *J* = 12 Hz, =CH), 7.3 (br s, 5); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.9, 27.4, 29.3, 66.3, 128.2, 128.4, 134.9, 135.9, 157.9, 167.3

(39) The percentage of **12** racemized due to deuterium loss in enolization = (98.4 − 84.7)/0.984 = 13.9%. If the deuterium isotope effect (k_H/k_D) is approximately 2 (see: Collins, C. J.; Bowman, N. S. "Isotope Effects in Chemical Reactions", Nostrand Reinhold: New York, 1970; p 277), then the percentage of racemization due to proton loss in enolization is = 2 × 13.9% = 27.8%, and the overall percentage of **12** racemized through enolization is 42%.

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(CO_2R); IR (neat) 1710 cm^{-1} (ester C=O). Anal. Calcd for $C_{22}H_{36}O_2Sn$: C, 58.56; H, 8.04. Found: C, 58.93; H, 8.09. Further elution gave 2.9 g (29%) of the *E* isomer: ^1H NMR ($CDCl_3$) δ 0.6–2.0 (m, 27), 5.1 (s, 2, CH_2O_2C); 6.3 (d, 1, J = 20 Hz, =CH), 7.3 (br s, 5), 7.8 (d, 1, J = 20 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 9.74, 13.7, 27.3, 29.0, 66.1, 128.0, 128.1, 128.3, 135.8, 153.1, 164.3 (CO_2R); IR (neat) 1720 cm^{-1} (ester C=O). Anal. Calcd for $C_{22}H_{36}O_2Sn$: C, 58.56; H, 8.04. Found: C, 58.69; H, 8.49.

1-(Tributylstannyl)-3-(*tert*-butyldimethylsiloxy)-1-propene. A mixture of 8.7 g (30 mmol) of tributyltin hydride, 5.1 g (30 mmol) of 3-(*tert*-butyldimethylsiloxy)-1-propyne,[3] and 50 mg (0.30 mmol) of azobis(isobutyronitrile) was slowly heated to 100 °C and maintained at 100 °C for 3 h. The reaction mixture was cooled, partitioned between ether and water, washed with aqueous sodium bicarbonate and brine, and then dried (Na_2SO_4). The solution was concentrated and distilled to give 9.6 g (72%) of product as a colorless liquid: bp 128 °C (0.1 mmHg); ^1H NMR ($CDCl_3$) δ 0.3 (s, 6, CH_3Si), 0.8–1.9 (m, 36), 4.3 (d, J = 2 Hz, CH_2O, *Z* isomer), 6.1 (s, 2, =CH, *E* isomer). The *E* to *Z* isomer ratio was 85:15. Anal. Calcd for $C_{21}H_{46}OSiSn$: C, 54.67; H, 10.05. Found: C, 54.17; H, 9.67.

1-Pentynyltributyltin. This compound was prepared by analogy to the preparation of (phenylethynyl)tributyltin[3] in 84% yield: bp 118–120 °C (1 mmHg); ^1H NMR ($CDCl_3$) δ 0.5–1.7 (m, 32), 2.2 (t, 2, J = 7 Hz, $\equiv CCH_2$); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.4, 13.7, 22.2, 22.6, 27.0, 29.0, 81.2 (≡CSn), 111.6 (≡C); IR (neat) 2100 cm^{-1} (C≡C); MS, *m/e* 301.0977. Anal. Calcd for $C_{13}H_{25}Sn$: (M − 57) 301.0976.

(Methoxymethyl)trimethyltin. Lithium trimethylstannate was prepared from 10.0 g (50.0 mmol) of trimethyltin chloride and 2.1 g (0.30 mmol) of lithium in 65 mL of THF.[58] The lithium trimethylstannate solution was transferred away from the excess lithium metal with a cannula, and cooled to 0 °C. To the solution was added 4.0 g (50 mmol) of chloromethyl methyl ether in 10 mL of THF, followed by stirring at ambient temperature for 12 h. The reaction mixture was quenched with 70 mL of water, and the aqueous layer was separated and washed with two 20-mL ether portions. The combined organic layer was washed with brine and then dried (Na_2SO_4) and distilled to give 4.2 g (41%) of (methoxymethyl)trimethyltin as a colorless liquid: bp 123 °C (650 mmHg) [lit.[59] bp 59.5 °C (65 mmHg)]; ^1H NMR ($CDCl_3$) δ 0.3 (s, 9, CH_3Sn), 3.2 (s, 3, CH_3O), 3.6 (s, 2, $SnCH_2O$); ^{13}C NMR ($CDCl_3$) δ −10.6 (CH_3Sn), 62.7, 65.0. The ^1H NMR spectrum matched the published data.[59]

(Methoxymethyl)tributyltin. This compound was made by a procedure analogous to that for the preparation of (methoxymethyl)trimethyltin;[59] however, the lithium tributylstannate was prepared from the reaction of tributyltin hydride with lithium diisopropylamide.[29] The product was purified by flash chromatography (silica gel), eluting with pentane to remove nonpolar side products, followed by methylene chloride to give (methoxymethyl)tributyltin, after removal of the solvent, in 41% yield: ^1H NMR ($CDCl_3$) δ 0.65–1.7 (m, 27), 3.3 (s, 3, CH_3O), 3.7 (s, 2, $SnCH_2O$); ^{13}C NMR ($CDCl_3$) δ 8.98, 13.7, 27.4, 29.2, 63.1, 64.3. Anal. Calcd for $C_{14}H_{32}OSn$: C, 50.18; H, 9.63. Found: C, 50.09; H, 9.37.

General Procedure for Preparation of Substituted Benzyltributyltin. To a mixture of 2.4 g (0.10 mol) of magnesium turnings in 40 mL of ether was added 0.100 mol of the desired substituted benzyl halide at such a rate to maintain a gentle reflux. When the addition was complete, the mixture was heated at the reflux temperature for 1 h and then cooled to room temperature. The Grignard solution was treated with a solution of 26 g (0.080 mol) of tributyltin chloride in 100 mL of benzene. As the addition proceeded, a white solid formed. When the addition was complete, the reaction mixture was heated at the reflux temperature for 12 h. The reaction mixture was quenched with 30 mL of saturated ammonium chloride, followed by 100 mL of water, giving two clear layers. The aqueous layer was separated and washed with 100 mL of ether. The combined organic layers were treated with anhydrous ammonia gas for 20 min; the resulting tributyltin chloride–ammonia complex was removed by filtration through a celite pad. The mother liquor was washed with water and brine, then dried (Na_2SO_4), concentrated, and distilled under reduced pressure to afford the desired substituted benzyltributyltin compound.

(3-(Trifluoromethyl)benzyl)tributyltin. This compound was prepared in 68% yield: bp 108 °C (0.05 mmHg); ^1H NMR ($CDCl_3$) δ 0.5–1.5 (m, 27), 2.15 (s, 2, $SnCH_2Ph$), 7.0 (s, 4); ^{13}C NMR ($CDCl_3$) δ 9.56, 13.5, 18.5, 27.5, 29.1, 119.6, 123.2, 128.4, 130.0, 132.2, 144.9. Anal. Calcd for $C_{20}H_{33}F_3Sn$: C, 53.48; H, 7.41. Found: C, 54.00, H, 7.57.

(3-Fluorobenzyl)tributyltin. This compound was prepared in 82% yield: bp 120–124 °C (0.04 mmHg); ^1H NMR ($CDCl_3$) δ 0.6–1.9 (m, 27), 2.3 (s, 2, $SnCH_2Ph$), 6.4–7.4 (m, 4); ^{13}C NMR ($CDCl_3$) δ 9.51, 13.8, 18.4, 27.4, 29.1, 109.5 (J_{CF} = 20 Hz), 113.4 (J_{CF} = 20 Hz), 122.5, 129.4 (J_{CF} = 9 Hz), 146.5 (J_{CF} = 9 Hz), 162.9 (CF, J_{CF} = 244.7 Hz). Anal. Calcd for $C_{19}H_{33}SnF$: C, 57.17; H, 8.33. Found: C, 57.07; H, 8.34.

(3-Methylbenzyl)tributyltin. This compound was prepared in 88% yield: bp 130 °C (0.07 mmHg); ^1H NMR ($CDCl_3$) δ 0.6–1.8 (m, 27), 2.3 (s, 5, $SnCH_2Ph$ and CH_3), 6.6–7.2 (m, 4); ^{13}C NMR ($CDCl_3$) δ 9.51, 14.0, 18.2, 21.5, 27.5, 29.2, 123.6, 124.0, 127.7, 128.0, 137.4, 143.2. Anal. Calcd for $C_{20}H_{36}Sn$: C, 60.79; H, 9.25. Found: C, 60.44; H, 9.18.

(4-Phenoxybenzyl)tributyltin. This compound was prepared from 4-(bromomethyl)diphenyl ether by a procedure analogous to that for the preparation of (4-methoxybenzyl)tributyltin[50] in 42% yield: bp 178–182 °C (0.07 mmHg); ^1H NMR ($CDCl_3$) δ 0.7–1.6 (m, 27), 2.3 (s, 2, $SnCH_2$), 6.8–7.4 (m, 9); ^{13}C NMR ($CDCl_3$) δ 9.39, 13.8, 17.4, 27.4, 29.1, 117.6, 119.6, 122.1, 127.9, 129.3, 138.8, 152.3, 158.2. Anal. Calcd for $C_{25}H_{38}OSn$: C, 63.45; H, 8.09. Found: C, 62.94; H, 7.88.

(3-Nitrobenzyl)tributyltin. A solution of 3.9 g (18 mmol) of 3-nitrobenzyl bromide,[60] 14.0 g (24.0 mmol) of hexabutylditin, and 0.20 g (0.18 mmol) of tetrakis(triphenylphosphine)palladium(0) in 100 mL of toluene was heated at the reflux temperature for 12 h, after which time there was a precipitate of palladium metal present. The reaction mixture was washed with 2 × 50 mL of aqueous potassium fluoride, concentrated, dissolved in ethyl acetate, and filtered through a pad of silica gel. The resulting mixture was purified by medium-pressure LC to give 3.4 g (44%) of (3-nitrobenzyl)tributyltin as a clear liquid: ^1H NMR ($CDCl_3$) δ 0.7–1.6 (m, 27), 2.4 (s, 2, $SnCH_2$), 7.2–7.4 (m, 2), 7.7 (m, 2); ^{13}C NMR ($CDCl_3$) δ 9.56, 13.7, 18.6, 27.4, 29.0, 117.8, 121.1, 128.8, 132.7, 146.3, 148.2. Anal. Calcd for $C_{19}H_{33}NO_2Sn$: C, 53.55; H, 7.81. Found: C, 53.95; H, 7.96.

General Procedure for Ketone Preparation Utilizing Derivatives of Trimethyltin in Chloroform. A solution of 5.0 mmol of the acid chloride and 15–20 mg ((2.0–2.6) × 10^{-2} mmol) of **1**[61] in 1 mL of chloroform was treated with 5.2 mmol of the organotin in 4 mL of chloroform. The yellow solution was heated at 65 °C with stirring under an air atmosphere in a tube sealed by a Teflon-brand vacuum stopcock, until palladium metal precipitated (1–24 h). The solution was cooled to room temperature, poured into 30 mL of ether, extracted with 2 × 20 mL of water, dried ($MgSO_4$), and concentrated. The residue was purified by chromatography or crystallization.

General Procedure for Ketone Preparation Utilizing Derivatives of Tributyltin in Chloroform. The reactions were conducted in the same fashion as with the organotrimethyltin compounds. After precipitation of palladium metal, the reaction mixture was poured into 30 mL of ether, washed with 30 mL of water and then with 30 mL of a half-saturated aqueous potassium fluoride solution with vigorous shaking, and allowed to stand 15–30 min. The resulting white precipitate of tributyltin fluoride was removed by filtration; the organic layer was separated and again washed with aqueous potassium fluoride. The second wash usually resulted in much less precipitation of tributyltin fluoride, from which the organic layer could be decanted. The organic layer was washed with brine and then dried ($MgSO_4$) and concentrated. The residue was treated with ethyl acetate, which resulted in additional tributyltin fluoride precipitate, which was removed by filtration with a celite pad. The mother liquor was purified by chromatography or crystallization.

Ketones. Ketones were synthesized on a preparative scale and identified by comparison with the known compounds or authentic samples. The ketones synthesized on a preparative scale were used in identifying the products of competitive reactions,, which were analyzed by HPLC. Comparisons were made with authentic commercially available samples of acetophenone, valerophenone, (*E*)-chalcone, α-methoxyacetophenone, and deoxybenzoin. The following known compounds were synthesized by the coupling procedure: 1-phenyl-2-propen-1-one,[62] 1,3-diphenylpropyn-1-one,[63] 1-phenyl-2-hexyn-1-one,[64] 4′-phenoxydeoxybenzoin,[65] 4′-methoxydeoxybenzoin,[66] 4′-methyldeoxybenzoin,[67] 3′-methyldeoxybenzoin,[68] 3′-fluorodeoxybenzoin,[69] 3′-(trifluoromethyl)deoxybenzoin,[70] and 3′-nitrodeoxybenzoin.[71]

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1-Phenyl-2-buten-1-one (6). This compound was prepared from benzoyl chloride and (*Z*)-propenyltributyltin according to the general procedure. The time of reaction was 4.5 h. The product was purified by flash chromatography to give the *E* isomer in 40% yield: ^{1}H NMR ($CDCl_3$) δ 1.97 (d, 3, J = 5.5 Hz, CH_3C=), 6.9–7.3 (m, 2, =CH), 7.3–7.6 (m, 3), 7.8–8.0 (m, 2); ^{13}C NMR ($CDCl_3$) δ 18.5 (CH_3), 127.2, 128.2, 132.3, 137.6, 144.6, 190.3 (C=O). Further elution of the column gave the *Z* isomer in 33% yield: ^{1}H NMR ($CDCl_3$) δ 2.1 (dd, 3, J = 7, 1.7 Hz, CH_3C=), 6.4 (dq, 1, J = 11.5, 7 Hz, CH=), 6.8 (dd, 1, J = 11.5, 1.7 Hz, CH=), 7.3–7.5 (m, 3), 7.8–8.0 (m, 2); ^{13}C NMR ($CDCl_3$) δ 16.1 (CH_3), 124.9, 127.9, 128.1, 132.2, 143.4, 191.4 (C=O); IR (neat) 1680 cm^{-1} (C=O). Anal. Calcd for $C_{10}H_{10}O$: C, 82.17; H, 6.90. Found: C, 81.35; H, 6.92. The ^{1}H NMR spectrum for each isomer matched the published data.[72]

2-Methyl-1-phenyl-2-buten-1-one. This compound was prepared from benzoyl chloride and a 25:75 mixture of (*E*)- to (*Z*)-2-butenyltributyltin according to the general procedure. The time of reaction was 72 h. The product was purified by medium-pressure LC (silica gel), by eluting with one column volume of hexane, followed by 1.5:98.5 ethyl acetate/hexane to give a 6% yield of valerophenone. Further elution gave the *E* isomer in 19% yield: ^{1}H NMR ($CDCl_3$) δ 1.5 (d, J = 7 Hz, =CCH_3), 1.95 (s, 3, =C(C=O)CH_3), 5.8 (q, J = 7 Hz, CH=), 7.3–7.7 (m, 5); ^{13}C NMR ($CDCl_3$) δ 15.2 (CH_3), 20.8 (CH_3), 126.3, 128.3, 128.7, 129.0, 132.7, 136.0, 199.7 (C=O); IR (neat) 1650 cm^{-1} (C=O). Further elution gave the *Z* isomer in 43% yield: ^{1}H NMR ($CDCl_3$) δ 1.8 (d, 3, J = 7 Hz, =CCH_3), 1.9 (s, 3, =C(C=O)CH_3), 6.4 (q, 1, J = 7 Hz, C*H*=), 7.3–7.7 (m, 5); ^{13}C NMR ($CDCl_3$) δ 11.9 (CH_3), 14.5 (CH_3), 127.6, 128.7, 130.8, 137.1, 138.4, 140.8, 198.0 (C=O); IR (neat) 1645 cm^{-1} (C=O). the ^{1}H NMR spectrum for the *Z* isomer matched the published data for an isomer of 2-methyl-1-phenyl-2-buten-1-one that was misassigned as the *E* isomer.[73]

The isomers were assigned by analogy to the relative shifts of the vinyl protons of the corresponding tin reagents. Also, the chemical shifts observed for the γ-methyl groups (*Z*, 1.8; *E*, 1.5) are consistent with the chemical shifts for (*E*)- and (*Z*)-1-phenyl-2-buten-1-one.[72] The ^{13}C chemical shifts for the γ-methyl carbons (*Z*, 11.9; *E*, 20.8) are consistent with these methyls being *Z* and *E*, respectively, to the carbonyl groups.[73,74]

(*E*)-Benzyl 4-Phenyl-4-oxo-2-butenoate (8). This compound was prepared by a modified general procedure utilizing 1.5 equiv of (*Z*)-benzyl 3-(tributylstannyl)propenoate and benzoyl chloride in the presence of 2 mol % of 1.[61] The time of reaction was 20 h. Purification was carried out by medium-pressure LC (silica gel, ethyl acetate/hexane, 10:90) to give the *E* isomer as a clear liquid in 55% yield: ^{1}H NMR ($CDCl_3$) δ 5.3 (s, 2, OCH_2Ph), 6.9 (d, 1, J = 16 Hz, C*H*=), 7.3–7.6 (m, 8), 7.8–8.0 (m, 3); ^{13}C NMR ($CDCl_3$) δ 67.0 (OCH_2), 128.1, 128.4, 128.6, 131.9, 135.1, 136.6, 165.0 (*C*O_2R), 189.0 (C=O); IR (neat) 1675 (C=O), 1725 (ester C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.51; H, 5.47.

(*Z*)-Benzyl 4-Phenyl-4-oxo-2-butenoate (8). This compound was prepared by the same procedure as for the *E* isomer; however, THF was used as the solvent instead of chloroform. The time of reaction was 16 h. Purification by medium-pressure LC (silica gel, ethyl acetate/hexane, 10:90), was carried out to give the *E* isomer in 58% yield. Further elution gave the *Z* isomer as a white solid in 28% yield: mp 67–68 °C; ^{1}H NMR ($CDCl_3$) δ 5.0 (s, 2, OCH_2Ph), 6.3 (d, 1, J = 12 Hz, C*H*=), 6.9 (d, 1, J = 12 Hz, CH=), 7.1–7.5 (m, 8), 7.8–7.9 (m, 2); ^{13}C NMR ($CDCl_3$) δ 66.7 (OCH_2), 125.3, 128.1, 128.2, 128.4, 133.4, 134.7, 135.4, 141.4, 164.2 (*C*O_2R), 193.6 (C=O); IR (KBr) 1675 (C=O), 1730 (ester C=O) cm^{-1}.

3-(*tert*-Butyldimethylsiloxy)-1-phenyl-2-propen-1-one. This compound was prepared from benzoyl chloride and an 85:15 mixture of (*E*)- to (*Z*)-1-(tributylstannyl)-3-(*tert*-butyldimethylsiloxy)-1-propene in the presence of 1% **1**[61] according to the general procedure. The time of reaction was 24 h. Purification was carried out by medium-pressure LC (silica gel, ethyl acetate/hexane, 5:95) to give the *E* isomer in 65% yield: ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 6, $SiCH_3$), 0.9 (s, 9, $SiCCH_3$), 4.4 (m, 2, CH_2O), 7.1 (br s, 2, =CH), 7.3–7.6 (m, 3), 7.9–8.1 (m, 2); ^{13}C NMR ($CDCl_3$) δ −5.4 ($SiCH_3$), 18.3, 25.8, 62.5 (CH_2O), 123.1, 128.2, 132.3, 137.6, 147.2, 189.7 (C=O); IR (neat) 1670 cm^{-1} (C=O); MS parent, *m/e* 276.1546, calculated for $C_{16}H_{24}O_2Si$, 276.1625. Further elution of the column gave the *Z* isomer in 12% yield: ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 6, CH_3), 0.9 (s, 9, $SiCCH_3$), 4.5 (m, 2, OCH_2), 5.8 (m, 1, CH=), 6.2 (m, 1, CH=), 7.3–7.6 (m, 3), 7.9–8.1 (m, 2).

The major isomer was determined to be *E* on the basis that the vinyl region was a broad singlet of two hydrogens, which is characteristic for other (*E*)-siloxypropenyltin[75] and (*E*)-hydroxypropenyltin[76] compounds. Comparison of the relative shifts for the siloxymethylene protons in 1-(tributylstannyl)-3-(*tert*-butyldimethylsiloxy)-1-propene, 4.2 ppm for *E* and 4.3 ppm for *Z*, to the relative shifts for the siloxymethylene group in the product, 4.4 ppm for the major isomer and 4.5 ppm for the minor isomer, was consistent with *E* being the major isomer, assuming that the signal is further upfield for the *E* isomer in both the tin reagent and the product ketone.

^{31}P NMR of the Coupling Reaction between Phenyltributyltin and Benzoyl Chloride in the Presence of 1. A solution of 300 mg (0.400 mmol) of **1**, 0.36 g (2.4 mmol) of benzoyl chloride, and 1.66 g (4.80 mmol) of phenyltributyltin in 4 mL of $CDCl_3$ was prepared, and approximately 3 mL of this solution was put in a 10-mm NMR tube. The reaction mixture was placed in the probe at 65 °C, and spectra were obtained intermittently (Figure 2). In a second experiment, the same reaction was run in the presence of an acetophenone internal standard. The reaction mixture was analyzed by HPLC (50% acetonitrile–water, 2 mL/min) and showed a 31% yield of benzophenone after 1 h and a 76% yield after 1.5 h.

Reaction of Tetramethyltin and 3 in Chloroform. (a) In the Absence of Added Triphenylphosphine. A solution of 100 mg (0.130 mmol) of **3** and 180 μL (232 mg, 0.130 mmol) of tetramethyltin in 0.5 mL of $CDCl_3$ was placed in an NMR tube. The yellow solution was heated at 65 °C under an air atmosphere. Palladium metal had precipitated within 9 h and the ^{1}H NMR of the reaction mixture showed complete conversion of tetramethyltin to a 70:30 mixture of acetophenone and toluene.

(b) In the Presence of Added Triphenylphosphine. A solution of 0.386 g (0.500 mmol) of **3**, 0.69 mL (0.89 g, 5.0 mmol) of tetramethyltin, and 0.262 g (1.00 mmol) of triphenylphosphine in 10 mL of chloroform was heated at 65 °C for 12 h. The reaction mixture was passed through a short alumina column (chloroform) and analyzed by HPLC (2% ethyl acetate/hexane, 2.0 mL/min). No acetophenone was observed relative to a deoxybenzoin internal standard.

Attempted Redistribution of Phenyltrimethyltin and Tetramethyltin in the Presence of 1. A solution of 90 mg (0.50 mmol) of tetramethyltin, 180 mg (0.500 mmol) of methyltriphenyltin, 140 mg (1.00 mmol) of benzoyl chloride, and 5 mg (7×10^{-3} mmol) of **1**[61] in 1 mL of $CDCl_3$ was heated at 65 °C in an NMR tube. Periodically the ^{1}H NMR spectrum of the reaction mixture was obtained. Through a reaction time of 20 h the ^{1}H NMR showed: 0.1 (s, Me_4Sn), 0.6 (s, Me_3SnCl), 0.7 (s, *Me*$SnPh_3$), 0.96 (s, *Me*$SnPh_2Cl$), 6.8–7.2 (m).

General Procedure for Competitive Coupling Reactions. A solution of 10–12 mg (0.013–0.016 mmol) of **1**[61] and 60 μL (72 mg, 0.51 mmol) of benzoyl chloride in 1 mL of solvent was treated with a mixture of 2.5 mmol each of the two tin reagents in 2 mL of solvent. The mixture was heated at 65 °C until palladium metal precipitated (1–12 h). The mixture was diluted with ether and passed through a celite pad. The mother liquor was analyzed by HPLC. The product ratio was determined by comparing the peak area of each ketone in the reaction mixture with the peak area observed in a mixture of the two expected ketone products present in known amounts.

General Procedure for the Competitive Coupling Reactions with Substituted Benzyltrialkyltin Compounds. Hammett Plot. A solution of 30 μL (36 mg, 0.26 mmol) of benzoyl chloride and 10 mg (0.013 mmol) of **1** in 0.5 mL of HMPA was treated with 0.95 g (2.5 mmol) of benzyltributyltin and 2.5 mmol of the substituted benzyltributyltin in 2.5 mL of HMPA. The reaction mixture was heated at 65 °C for approximately 12 h, quenched with ether, and filtered through a celite pad to remove the palladium metal. The reaction mixture was analyzed by HPLC to determine the product ratio by comparison to a mixture of known amounts of the two expected ketones.

Coupling of (*Z*)-Styryltrimethyltin with Benzoyl Chloride. (a) Standard Conditions. A solution of 0.83 g (3.1 mmol) of a 15:85 mixture of (*E*)- and (*Z*)-styryltrimethyltin, 0.35 mL (0.42, 3.0 mmol) of benzoyl chloride, and 12 mg (0.015 mmol) of **1** in 2 mL of chloroform was heated for 5.5 h. The mixture was then diluted with 8 mL of ether and filtered through a celite pad. The reaction mixture was analyzed by HPLC (50% acetonitrile–water, 2 mL/min) and showed only (*E*)-chalcone (retention time = 11.5 min), by comparison to a mixture of (*E*)- and (*Z*)-chalcone,[77] each present in known amounts.

(b) In the Presence of 2,6-Di-*tert*-butylphenol. The reaction was carried out under normal conditions; with the exception that 10 mol % of 2,6-di-*tert*-butylphenol was added. The reaction was heated at 65 °C

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for 17 h, diluted with ether, filtered through a celite pad, and analyzed by HPLC (50% acetonitrile–water). A 34:66 mixture of (*E*)- and (*Z*)-chalcone (retention time = 11.5 min) was observed by comparison to a mixture of (*E*)- and (*Z*)-chalcone[77] present in known amounts.

Coupling of (*Z*)-2-Propenyltributyltin with Benzoyl Chloride. A solution of 1.03 g (3.10 mmol) of (*Z*)-2-propenyltributyltin, 0.35 mL (0.42 g, 3.0 mmol) of benzoyl chloride, and 12 mg (0.015 mmol) of **1** in 3 mL of chloroform was heated at 65 °C. After 1 h an 0.8-mL aliquot was removed, concentrated, diluted with 10% ethyl acetate/hexane, and filtered through a small pad of silica gel. The filtered solution was concentrated, diluted with chloroform, and analyzed by GC [10% OV-101 Chromosorb W-8/100, 2 m × $^1/_8$ in., 30 mL/min, 100 °C (5 min) then 10 °C/min to 160 °C]. The GC analysis showed a 1.1:1 mixture of (*E*)- to (*Z*)-1-phenyl-2-buten-1-one. The retention time for the *Z* isomer was 9.9 min, for the *E* isomer was 10.5 min. An aliquot was removed after 2 h and handled similarly, with a 0.9:1 mixture of *E* and *Z* isomers being observed. After 4.5 h a similar analysis showed a 1:1 mixture of *E* and *Z* isomers.

(*S*)-(−)-(α-Deuteriobenzyl)tributyltin (11). To 1.70 mL (1.23 g, 12.3 mmol) of diisopropylamine in 20 mL of THF at 0 °C was added 6.85 mL (10.6 mmol) of a 1.55 M hexane solution of *n*-butyllithium. After the mixture was stirred at 0 °C for 30 min, 2.86 mL (3.09 g, 10.6 mmol) of tributyltin hydride was added by syringe and the mixture was stirred at 0 °C for 30 min, resulting in a gold solution. The lithium tributylstannate solution was added to a solution of 1.42 g (11.2 mmol) of (*R*)-(−)-benzyl-α-*d* chloride,[28] (**10**-*R*) $[\alpha]^{20}_D$ −1.15°, 75% ee [prepared[27] from *S*-(+)-benzyl-α-*d* alcohol (**9**-*S*) $[\alpha]^{20}_D$ 1.33 (neat, *l* = 1), 84% ee] in 22 mL of THF at 0 °C over a period of 30 min. The reaction mixture was kept at 0 °C for 5 h and was then quenched with 40 mL of water. The mixture was extracted with 50 mL of ether, which was separated and washed with water and brine. The ether extract was dried ($MgSO_4$), concentrated, and purified by medium-pressure LC (silica gel, hexane) to give 3.42 g (84%) of **11**-*S* as a clear colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.7–1.6 (m, 27), 2.3 (br s, 1, CHDSn), 6.9–7.3 (m, 5); ^{13}C NMR ($CDCl_3$) δ 9.39, 13.8, 18.0 (t, J_{CD} = 19 Hz, CD), 27.4, 29.1, 122.7, 126.9, 128.2, 143.5; $[\alpha]^{20}_D$ −0.328°, $[\alpha]^{20}_{436}$ −0.790° (neat).

(*R*)-(−)-α-Deuteriobenzyl Phenyl Ketone. A solution of 1.41 g (10.0 mmol) of benzoyl chloride, 3.92 g (10.3 mmol) of **11**-*S*, and 303 mg (0.400 mmol) of **1** in 10 mL of HMPA was heated at 65 °C for 16 h. The reaction mixture was poured into 40 mL of ether and was washed with 3 × 30 mL of water, followed by 40 mL of saturated aqueous potassium fluoride. The aqueous layer was separated and the tributyltin fluoride precipitate was removed by filtration. The mother liquor was concentrated, treated with ethyl acetate, and filtered through a celite pad. The product mixture was purified by radial chromatography (silica gel, ethyl acetate/hexane, 10:90) to give 1.4 g (71%) of **12**-*R* as a white solid: mp 51–52 °C; ^{1}H NMR ($CDCl_3$) δ 4.2 (t, 1, J_{CHD} = 1.7 Hz, CD*H*), 7.2–7.5 (m, 3), 7.8–8.0 (m, 2); ^{13}C NMR ($CDCl_3$) δ 44.95 (t, J_{CD} = 19 Hz, *C*D), 126.5, 128.3, 129.1, 132.8, 134.2, 136.1, 197.1 (C=O); $[\alpha]^{20}_D$ −0.314°, $[\alpha]^{20}_{436}$ −0.772° (CCl_4, *c* 30.3).

Preparation of 12-*R* from 3 and 11-*S*. A solution of 1.45 g (3.80 mmol) of **11**-*S* ($[\alpha]^{20}_D$ −0.235°) and 2.82 g (3.65 mmol) of **3** in 9 mL of HMPA was heated at 65 °C. After 1.5 h there was palladium metal present, and the reaction was poured into 50 mL of ether. The ether layer was washed with 3 × 50 mL of water, filtered through a celite pad, and chromatographed on a 10-cm column (silica gel, ether). The ether layer was washed with saturated aqueous potassium fluoride, allowed to stand 30 min, and the precipitate was removed by filtration. The mother liquor was concentrated and treated with ethyl acetate. The resulting precipitate was removed by filtration. The filtrate was dried ($MgSO_4$), concentrated, and purified by radial chromatography (silica gel, ethyl acetate/hexane, 10:90) to give 210 mg (30%) of **12**-*R* as a white solid: $[\alpha]^{20}_D$ −0.12°, $[\alpha]^{20}_{436}$ −0.28° (CCl_4, c 9.9).

(*R*)-(−)-α-Deuteriobenzyl Benzoate (13). This compound was prepared from **12**-*R* by a Baeyer–Villiger oxidation.[35] A solution of 450 mg (2.28 mmol) of **12**-*R* in 5 mL of chloroform was treated with 0.11 mL of boron–trifluoride etherate, followed by the dropwise addition of a mixture of 693 mg (3.60 mmol) of 40% aqueous peracetic acid in 2 mL of chloroform. The reaction mixture was treated with 10 mL of 25% aqueous sodium sulfite and stirred for 30 min. The mixture was treated with 20 mL of chloroform, and the organic layer was separated and washed with water, saturated aqueous sodium bicarbonate, water, and brine. The organic layer was dried ($MgSO_4$), concentrated, and purified by medium-pressure LC (silica gel, ethyl acetate/hexane, 5:95) to give 220 mg (46%) of **13**-*R* as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 5.3 (br s, 1, OCHD), 7.3–7.5 (m, 8), 8.0–8.2 (m, 2); $[\alpha]^{20}_D$ −0.10°, $[\alpha]^{20}_D$ −0.310° (CCl_4, *c* 9.0); MS, *m/e* (relative intensity) 213 (20), 105 (100), 92 (38), 77 (25), 32 (33), 28 (100).

(*S*)-(+)-α-Deuteriobenzyl Benzoate (13). A solution of 700 mg (6.41 mmol) of **9**-*S* ($[\alpha]^{20}_D$ 1.33°, 85% ee) in 5 mL of pyridine at 0 °C was treated with 1.00 g (7.11 mmol) of benzoyl chloride. The solution was heated at 60 °C for 1 h and then poured into 40 mL of water. The aqueous layer was extracted with 40 mL of ether, which was washed with 2 × 40 mL of 10% aqueous hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water. The ether layer was dried ($MgSO_4$), concentrated, and purified by medium-pressure LC (silica gel, ethyl acetate/hexane, 5:95) to give 1.16 g (85%) of **13**-*S* as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 5.3 (br s, 1, OCHD), 7.3–7.5 (m, 8), 8.0–8.2 (m, 2); $[\alpha]^{20}_D$ 0.36°, $[\alpha]^{20}_{365}$ 1.26°, 84% ee; MS, *m/e* (relative intensity) 213 (35), 105 (100), 92 (69), 77 (35), 32 (34), 28 (100).

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Registry No. 1, 86633-24-1; **3**, 29158-91-6; (*E*)-**6**, 35845-66-0; (*Z*)-**6**, 35660-91-4; (*Z*)-**7**, 86633-18-3; (*E*)-**7**, 86633-19-4; (*E*)-**8**, 86633-20-7; (*Z*)-**8**, 86633-21-8; (*S*)-(+)-**9**, 3481-15-0; (*R*)-(−)-**10**, 4181-91-3; (*S*)-(−)-**11**, 84369-11-9; (*R*)-(−)-**12**, 84369-12-0; (*R*)-(−)-**13**, 84369-13-1; (*S*)-(+)-**13**, 84369-14-2; PhCOCl, 98-88-4; Me_3SnEt, 3531-44-0; Bu_3Sn-*i*-Pr, 41728-45-4; Me_2SnBu_2, 1528-00-3; Me_3SnPh, 934-56-5; Bu_3SnPh, 960-16-7; $Ph_3(Me)Sn$, 1089-59-4; Me_4Sn, 594-27-4; (*E*)-Me_3SnCH=CHPh, 7422-28-8; (*E*)-Bu_3SnCH=CHPh, 66680-88-4; (*E*)-Ph_3SnCH=CHPh, 57682-80-1; O_2N-*m*-$C_6H_4CH_2SnBu_3$, 79159-73-2; F_3C-*m*-$C_6H_4CH_2SnBu_3$, 86633-10-5; F-*m*-$C_6H_4CH_2SnBu_3$, 86633-11-6; $PhCH_2SnBu_3$, 28493-54-1; Me-*m*-$C_6H_4CH_2SnBu_3$, 86633-12-7; Me-*p*-$C_6H_4CH_2SnBu_3$, 74260-32-5; MeO-*p*-$C_6H_4CH_2SnBu_3$, 74260-40-5; PhO-*p*-$C_6H_4CH_2SnBu_3$, 86633-13-8; (*Z*)-Me_3SnCH=CHPh, 17421-57-7; (*E*)-$Bu_3SnC(CH_3)$=$CHCH_3$, 86633-14-9; (*Z*)-$Bu_3SnC(CH_3)$=$CHCH_3$, 86633-15-0; (*E*)-Bu_3SnCH=$CHCH_2OSi$(Bu-*t*)Me_2, 86633-16-1; (*Z*)-Bu_3SnCH=$CHCH_2OSi$(Bu-*t*)Me_2, 86646-19-7; PhC≡$CSnMe_3$, 1199-95-7; PhC≡$CSnBu_3$, 3757-88-8; *n*-PrC≡$CSnMe_3$, 1118-50-9; *n*-PrC≡$CSnBu_3$, 86633-17-2; CH_2=$CHSNBu_3$, 7486-35-3; CH_2=$CHSnMe_3$, 754-06-3; $CH_3OCH_2SnMe_3$, 4649-80-3; $SnBu_4$, 1461-25-2; Bu_3SnLi, 4226-01-1; Bu_3SnCl, 1461-22-9; (*E*)-β-bromostyrene, 588-72-7; (*Z*)-β-bromostyrene, 588-73-8; trimethyltin chloride, 1066-45-1; benzyl propiolate, 14447-01-9; tributyltin, 688-73-3; 3-(*tert*-butyldimethylsiloxy)-1-propene, 76782-82-6; lithium trimethylstannate, 17946-71-3; chloromethyl methyl ether, 107-30-2; (methoxymethyl)tributyltin, 27490-32-0; phenylacetylene, 536-74-3; propenyl bromide, 590-14-7; (*Z*)-1-propenyltrimethyltin, 4964-06-1; 2-chloro-2-butene, 4461-41-0; 3-nitrobenzyl bromide, 3958-57-4; hexabutylditin, 813-19-4; (*E*)-2-methyl-1-phenyl-2-buten-1-one, 20047-50-1; (*Z*)-2-methyl-1-phenyl-2-buten-1-one, 20047-49-8; (*E*)-3-(*tert*-butyldimethylsiloxy)-1-phenyl-2-propen-1-one, 86633-22-9; (*Z*)-3-(*tert*-butyldimethylsiloxy)-1-phenyl-2-propen-1-one, 86633-23-0.

Supplementary Material Available: ^{31}P NMR spectra of **1** and **3** observed in the reaction between phenyltributyltin and benzoyl chloride in the presence of **1** (catalytic cycle) (1 page). Ordering information is given on any current masthead page.