Palladium-Catalyzed Carbamoylation and Alkoxycarbonylation of Vinyl- and Arylorganotins: An Easy Entry into Vinyl or Aryl Amides and Esters†

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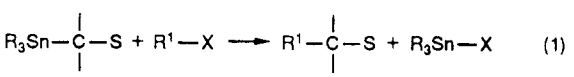
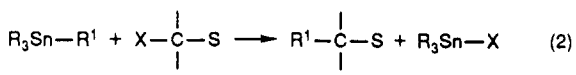
Summary: The palladium-catalyzed cross-coupling reaction between substituted aryl- and vinylorganotins or heterocyclic organotin compounds and chloroformates or carbamoyl chlorides is reported. It proceeds smoothly to provide esters or amides in good yields. The reaction conditions are mild, and a wide range of functionalities on the tin reagent can be tolerated.

One-carbon homologation is an important step in organic synthesis. Among the methods available for the addition of a functional group to a vinyl or aryl group, organometallic routes are often very convenient.[1] Since Bouveault's first report,[2] one of the most popular ways involves coupling between carbanions and formic acid derivatives. However, the high reactivity of carbanions sometimes makes this procedure untenable because of their incompatibility with other functional groups present in the starting materials. Milder zinc[3] or aluminum[4] derivatives, which couple with chloroformates to give esters, are limited to nonfunctional alkyl or vinyl compounds. Tedious protection–deprotection processes are then necessary. Due to the increasing complexity of target molecules in organic synthesis, selective methods for the introduction of a functional carbon are thus essential. The relative weakness of the tin–carbon bond allows the direct transfer of an organic moiety from the metal to organic substrates under mild conditions, in the presence of numerous functional groups.[5] Some examples of one-carbon transfer (eq 1) are known, such as the transfer of an hydroxy,[6] methoxymethyl,[7] or dialkylamido[8] group to aryl bromides, of a trichloromethyl group to aldehydes,[9] and of a (dialkylamino)methyl group to acyl chlorides[10] or aldehydes.[11]



$$R_3Sn-\overset{|}{\underset{|}{C}}-S + R^1-X \longrightarrow R^1-\overset{|}{\underset{|}{C}}-S + R_3Sn-X \qquad (1)$$

Formylation is possible by the reaction of aryl halides with tin hydrides in the presence of carbon monoxide.[12] A further procedure for one-carbon homologation via organotin reagents is the transfer of an organic group from the tin to the functional carbon (eq 2).



$$R_3Sn-R^1 + X-\overset{|}{\underset{|}{C}}-S \longrightarrow R^1-\overset{|}{\underset{|}{C}}-S + R_3Sn-X \qquad (2)$$

This route includes trichloromethylation of vinyltins,[13] alkoxycarbonylation of 2-pyrrolyltins,[14] and (dialkylamino)methylation[15] or formylation[16] of aryltins. Nevertheless, the introduction of an alkoxycarbonyl group is limited to reactive organotins. Futhermore, their carbamoylation has not yet been reported. Since Stille's reports[17] of palladium-catalyzed coupling of organotins with halides, the scope of applications of organotins to carbon–carbon bond formation has been considerably broadened[18] because of the versatility of this mild method of elaboration of carbon–carbon bonds. We report here the preparation of esters or amides by palladium-catalyzed coupling of vinyl- or arylorganotins with chloroformates or carbamoyl chlorides.

The first coupling reactions attempted, with use of isobutyl chloroformate and *p*-tolyltributylstannane under standard conditions, were very disappointing. At 80 °C in toluene, reaction of *p*-tolyltributyltin, 2 mol % $(PPh_3)_2PdCl_2$, and 1.2 equiv of isobutyl chloroformate gave after 4 h isobutyl *p*-methylbenzoate in only 20% yield, together with an 18% yield of di-*p*-tolyl ketone. Replacing toluene by chloroform increased the yield of di-*p*-tolyl ketone to 52%. Heating to 60 or 100 °C for 2–60 h with or without added phosphine or with $Pd(PPh_3)_4$, (benzyl)$ClPd(PPh_3)_2$, or ligand-free palladium catalyst[12,19] did not improve the yield of desired product. In these experiments, the presence of high amounts of di-*p*-tolyl ke-

† This paper is dedicated to the memory of the late Professor J. K. Stille.

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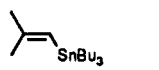
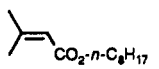
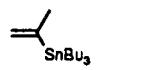
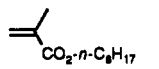
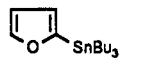
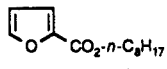
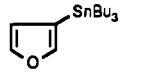
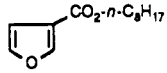
Table I. Coupling of Tin Reagents with Chloroformates

entry no.	tin reagent	product	% yield[a]
1	$PhSnBu_3$	$PhCO_2$-*i*-C_4H_9	66
2	*p*-$MeC_6H_4SnBu_3$	*p*-$MeC_6H_4CO_2$-*i*-Bu	64
3	*p*-$MeOC_6H_4SnBu_3$	*p*-$MeOC_6H_4CO_2$-*i*-Bu	66
4	*p*-$MeOCOC_6H_4$-$SnBu_3$	*p*-$MeOCOC_6H_4CO_2$-*i*-Bu	72
5	*p*-$Me_2NC_6H_4$-$SnBu_3$	*p*-$Me_2NC_6H_4CO_2$-*i*-Bu	88[31]
6	*p*-$Me_2NC_6H_4$-$SnBu_3$	*p*-$Me_2NC_6H_4CO_2Et$	71[32]
7			70
8			47[33]
9			70
10			83

[a] Yields are isolated yields.

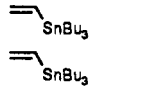
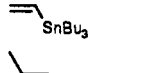
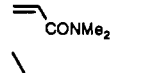
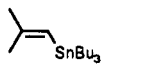
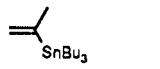
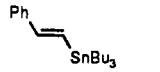
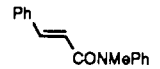
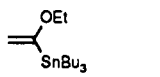
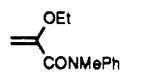
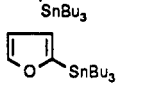
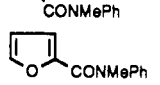
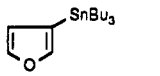
tone indicated clearly that a decomposition of chloroformates to phosgene occurred, leading to the symmetrical ketone. Such a pathway has been suggested to explain the formation of acetone from oxalyl chloride and tetramethyltin.[20a] Subsequently, we checked the stability of phenyl and isobutyl chloroformates under the reaction conditions and found that they were rapidly decomposed into carbonates and presumably phosgene[21] by the catalyst. The experimental conditions then were modified in order to lower the contact time between the catalyst and chloroformates. The amount of palladium complex also was decreased to 0.5 mol %, and HMPA (10%) was added to increase the reaction rate.[20b] The very slow addition of a solution of the chloroformate and (benzyl)ClPd(PPh_3)$_2$ in toluene to the tin reagent in toluene and HMPA at 100 °C resulted in a remarkable improvement in yield; isobutyl *p*-methylbenzoate was isolated in triple the original yield (eq 3).

$$Bu_3Sn\text{–}R^1 + ClCO_2R^2 \rightarrow R^1\text{–}CO_2R^2 + Bu_3Sn\text{–}X \quad (3)$$

The reaction then was extended to arylstannanes bearing functional groups such as ethers, tertiary amines, or esters. There was no interference of these groups with the coupling reaction, as generally observed. Vinyltins and 2- and 3-furyltributylstannanes were also substrates for such reactions. Allytins did not provide the corresponding esters with chloroformates in good yields. Now hydroquinone was added to the reaction mixture to limit polymerization of the reactive acrylates formed. The influence of the alkoxy group on the chloroformate was also studied (Table I, entries 5 and 6): isobutyl chloroformate was found to give better yields than ethyl chloroformate.

The coupling reaction of organostannanes and carbamoyl chlorides also was investigated. In this study solid *N*-methyl-*N*-phenylcarbamoyl chloride was prefered to toxic, low-boiling, commercial *N*,*N*-dimethylcarbamoyl

Table II. Coupling of Tin Reagents with Carbamoyl Chlorides

entry	tin reagent	product	% yield[a]
1	$PhSnBu_3$	PhCONMePh	81
2	$PhSnBu_3$	$PhCONMe_2$	72
3	*p*-$MeC_6H_4SnBu_3$	*p*-$MeC_6H_4CONMePh$	48[34]
4	*p*-$MeOC_6H_4SnBu_3$	*p*-$MeOC_6H_4CONMePh$	57[34]
5	*p*-$Me_2NC_6H_4SnBu_3$	*p*-$Me_2NC_6H_4CONMePh$	50[34]
6			74[35]
7			71
8			60[36]
9			71[37]
10			67
11			65
12			68[38]
13			73[38]
14	(allyl)$SnBu_3$	(allyl)CONMePh	18[39,b]

[a] Yields are isolated yields. [b] The main product is allylmethylphenylamine (see text).

chloride because of its low volatility. When *N*-methyl-*N*-phenylcarbamoyl chloride was treated with arylstannanes, the coupling proceeded smoothly to furnish the desired amides (Table II, entry 1). *N*-Methyl-*N*-phenylcarbamoyl chloride was found to be far more stable than chloroformates under the reaction conditions, such that HMPA was not necessary and the reagents could be mixed together before heating. Substituted arylstannanes gave somewhat lower yields (Table II, entries 3–5), and coupling was not observed with (*p*-(methoxycarbonyl)phenyl)tributylstannane, where an ester group is present on the aromatic ring, even with added HMPA. Substituted acrylic amides were obtained from substituted vinylstannanes in satisfactory yields (Table II, entries 6 and 8–11), as were *N*-methyl-*N*-phenyl-2-furyl or *N*-methyl-*N*-phenyl-3-furyl amide (Table II, entries 12 and 13) (eq 4).

$$Bu_3Sn\text{–}R^1 + ClCONR^2_2 \rightarrow R^1\text{–}CONR^2_2 + Bu_3Sn\text{–}X \quad (4)$$

When a mixture of (*E*)- and (*Z*)-2-(tributylstannyl)-styrene (80/20; Table II, entry 20) was reacted with *N*-methyl-*N*-phenylcarbamoyl chloride, only (*E*)-*N*-methyl-*N*-phenyl-3-phenylpropenamide was formed. Palladium-catalyzed coupling reactions between acyl chlorides and (*Z*)-vinyltins resulted in the *E* conjugated ketone after isomerization of the initially formed *Z* conjugated ketone,[20b] and such isomerization is presumed to take place here. This coupling is not specific to *N*-methyl-*N*-phenylcarbamoyl chloride; satisfactory results were obtained with dimethylcarbamoyl chloride (Table II, entry 7). Together with the desired product, we always isolated variable amounts (5–30%) of *N*-methyl-*N*-phenylurea, indicating some decomposition of the carbamoyl chloride during the reaction. This byproduct was easily separated from the amides by column chromatography. With (2-acetyl-1,4-cyclohexadienyl)tributylstannane, we did not observe any coupling, whereas the same compound reacted with benzoyl chloride;[18d] as with (*p*-(methoxycarbonyl)-

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phenyl)tributylstannane, a carbonyl group does not seem suitable for the coupling. The use of a ligand-free palladium catalyst did not improve the yield. Reaction with allyltributylstannane gave the corresponding *N*-methyl-*N*-phenyl-3-butenamide in only 18% yield, together with a 45% yield of *N*-allyl-*N*-methylaniline.

In conclusion, we have demonstrated the utility of the palladium-catalyzed cross-coupling of chloroformates and carbamoyl chlorides with aryl or vinylstannanes, especially when aryl- or vinylstannanes were accessible by a noncarbanionic route, i.e., by coupling hexabutylditin with iodoarenes[27,28] or by hydrostannylation or cuprostannylation of acetylenic compounds.[3] One-carbon homologation from organotins thus was achieved to give esters or amides in good yields.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Toluene, THF, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. HMPA was distilled from CaH_2 and stored on molecular sieves (4 Å). $CHCl_3$ was passed through a short basic alumina column before use. PCl_5, hydroquinone, isobutyl, *n*-octyl, and phenyl chloroformates, and dimethylcarbamoyl chloride were used as received. Vinyltin,[22] ((*Z*)-methyl-1-propenyl)tributyltin,[23] (1-methyl-1-ethenyl)tributyltin,[24] styryltributyltin,[24] phenyltributyltin,[24] (*p*-methoxyphenyl)tributyltin,[25] (*p*-(dimethylamino)phenyl)tributyltin,[24] *p*-tolyltributyltin,[25] and allyltributyltin[24] were prepared from the corresponding Grignard reagents. (2-Ethoxy-1-ethenyl)tributyltin[26] and 3-(tributylstannyl)furan[23] were obtained from the corresponding lithium derivatives. 4-(Tributylstannyl)benzonitrile[27] and methyl 4-(tributylstannyl)benzoate[28] were prepared from 4-bromobenzonitrile or methyl 4-bromobenzoate and hexabutylditin. ^1H NMR spectra were recorded on a Perkin-Elmer-Hitachi R24 or a Bruker WH 250 spectrometer (solvent $CDCl_3$, internal reference Me_4Si).

***N*-Methyl-*N*-phenylcarbamoyl Chloride.**[29,30] To a cooled (−20 °C) solution of butyllithium (0.25 mol) in hexane (2.5 N) was added distilled *N*-methylaniline (26.8 g, 0.25 mol) with stirring. After 1 h at room temperature, 100 mL of dry THF was added. CO_2 (gas) was then introduced slowly until the exothermal reaction stopped. Me_3SiCl (27.16 g, 0.25 mol) diluted in 20 mL of dry THF was added, and the mixture was heated to reflux for 3 h. After evaporation of the solvent, extraction of the residue with dry petroleum ether, and evaporation of the solvent, trimethylsilyl *N*-methyl-*N*-phenylcarbamate was obtained (49.6 g, 89% yield). PCl_5 (46.4 g, 0.22 mol) was dissolved in 400 mL of dry $CHCl_3$ and the solution cooled at 0 °C. The carbamate (49.6 g, 0.22 mol) was added dropwise. After 2 h at room temperature, the mixture was filtered. The solvent was evaporated and the solid recrystallized from dry diethyl ether (29.8 g, 80% yield); mp 87 °C.

Procedure for Coupling Reactions of Chloroformates and Organotins. To a solution of tin reagent (5 mmol) and a few crystals of hydroquinone in a mixture of dry toluene (20 mL) and HMPA (5 mL) at 100 °C was added over 4 h a solution of benzylchlorobis(triphenylphosphine)palladium (0.025 mmol, 20 mg) and chloroformate (5 mmol) in 20 mL of toluene. The mixture was heated to 100 °C for an additional 1 h before being cooled and partitioned between 100 mL of ethyl acetate and 50 mL of a saturated solution of KF in water. The precipitate of tributyltin fluoride was removed by filtration, the organic layer was separated, the solvents were evaporated, and the residue was extracted with 50 mL of acetonitrile. After filtration and evaporation of the solvent, the products were isolated by liquid chromatography on a silica gel column (petroleum ether/diethyl ether, 95/5).

Procedure for Coupling Reactions of *N*-Methyl-*N*-phenylcarbamoyl Chloride and Organotins. A solution of the organotin compound (5 mmol), carbamoyl chloride (850 mg, 5 mmol), and dichlorobis(triphenylphosphine)palladium (140 mg, 0.2 mmol) under nitrogen was heated at 100 °C until it turned black (2–8 h). It was then treated as above and purified by chromatography on a silica gel column (petroleum ether/diethyl ether, 80/20). Coupling products (^1H NMR (δ); mass spectrum (positive ion, EI, m/e)) are as follows. Isobutyl benzoate: 8.0 (2 H, m), 7.4 (3 H, m), 4.06 (2 H, d, $^3J_{HH}$ = 7 Hz), 2.08 (1 H, m), 1.0 (6 H, d); 123 ($PhCO_2H_2^+$, 0.4), 105 ($M^+ - C_4H_9O$, 1). Isobutyl *p*-methylbenzoate: 7.9 (2 H, d), 7.1 (2 H, d), 4.05 (2 H, d, $^3J_{HH}$ = 7 Hz), 2.32 (3 H, s), 2.09 (1 H, m), 1.02 (6 H, d); 137 ($CH_3C_6H_4O_2H_2^+$, 0.4), 136 (M^+ - butene, 0.2), 119 ($M^+ - C_4H_9O$, 1). Isobutyl *p*-methoxybenzoate: 7.9 (2 H, d), 6.80 (2 H, d), 4.05 (2 H, d, $^3J_{HH}$ = 7 Hz), 3.23 (3 H, s), 2.05 (1 H, m), 1.01 (6 H, d); 208 (M^+, 0.12), 152 (M^+ - butene, 0.75), 135 ($M^+ - C_4H_9O$, 1). Isobutyl *p*-carbomethoxybenzoate: 8.09 (4 H, s), 4.13 (2 H, d, $^3J_{HH}$ = 7 Hz), 3.94 (3 H, s), 2.07 (1 H, m), 1.03 (6 H, d); 205 ($M^+ - CH_3O$, 0.1), 181 ($MeCOC_6H_4CO_2H_2^+$, 0.55), 163 ($M^+ - C_4H_9O$, 1). Isobutyl *p*-(dimethylamino)benzoate: 7.78 (2 H, d), 6.49 (2 H, d), 3.95 (2 H, d), 2.91 (6 H, s), 1.94 (1 H, m), 0.97 (6 H, d); 221 (M^+, 0.6), 165 (M^+ - butene, 0.9), 164 ($M^+ - C_4H_9$, 0.6), 148 ($M^+ - C_4H_9O$, 1). *n*-Octyl 3-methyl-2-butenoate: 5.57 (1 H, s), 3.96 (2 H, t, $^3J_{HH}$ = 6 Hz), 2.12 (3 H, s), 1.87 (3 H, s), 1.30 (12 H, m), 0.90 (3 H, t); 212 (M^+, 0.05), 101 ($C_4H_7CO_2H_2^+$, 0.6), 100 ($C_4H_7CO_2H^+$, 0.8), 83 ($C_4H_7CO^+$, 1). *n*-Octyl 2-furoate: 7.52 (1 H, s), 7.06 (1 H, d, $^3J_{HH}$ = 3 Hz), 6.40 (1 H, q), 4.20 (2 H, t, $^3J_{HH}$ = 6 Hz), 1.30 (12 H, m), 0.89 (3 H, t); 224 (M^+, 0.04), 157 ($M^+ - C_8H_{17}$, 1), 113 ($M^+ - C_5H_3O_3$, 0.6). *n*-Octyl 3-furoate: 7.83 (1 H, s), 7.30 (1 H, s), 6.62 (1 H, s), 4.11 (2 H, t, $^3J_{HH}$ = 6 Hz), 1.30 (12 H, m), 0.89 (3 H, t); 224 (M^+, 0.06), 113 ($C_8H_{17}^+$, 0.5), 112 ($C_8H_{16}^+$, 0.5), 95 ($C_5H_3O^+$, 1). *N*-Methyl-*N*-phenyl-2-ethoxypropenamide: 7.10 (5 H, s), 4.63 (1 H, s, $^2J_{HH}$ = 2 Hz), 4.08 (1 H, s, $^2J_{HH}$ = 2 Hz), 3.30 (2 H, q, $^3J_{HH}$ = 7 Hz), 3.22 (3 H, s), 0.72 (4 H, t, $^3J_{HH}$ = 7 Hz); 205 (M^+, 0.8), 176 ($M^+ - C_2H_5$, 0.5), 160 ($M^+ - C_2H_5O$, 0.6), 148 ($M^+ - C_3H_5O$, 0.5), 134 ($M^+ - C_5H_7O_2$, 0.8), 77 ($C_6H_5^+$, 1). *N*-Methyl-*N*-phenyl-3-phenylpropenamide: 7.58 (1 H, d, $^3J_{HH}$ = 15.5 Hz), 7.37 (10 H, m), 6.28 (2 H, d, $^3J_{HH}$ = 15.5 Hz), 3.31 (3 H, s); 238 (M^+, 0.05), 134 ($M^+ - C_8H_7$, 1), 106 ($PhNMe^+$, 0.8). *N*-Methyl-*N*-phenylbenzamide: 7.02 (10 H, m), 3.35 (3 H, s); 211 (M^+, 0.3), 105 ($M^+ - C_7H_8N$, 1), 77 (C_6H_5, 0.5). *N*,*N*-dimethylpropenamide: 6.67 (1 H, q, $^3J_{HH}$ = 17 Hz, $^3J_{HH}$ = 10 Hz), 6.08 (1 H, q, $^3J_{HH}$ = 17 Hz, $^2J_{HH}$ = 3 Hz), 5.52 (1 H, q, $^3J_{HH}$ = 10 Hz, $^2J_{HH}$ = 3 Hz); 99 (M^+, 0.3), 98 (M^+ - H, 0.5), 55 ($M^+ - C_2H_6N$, 1).

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