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N-Heterocyclic carbene catalyzed oxidative stannylation of aldehydes: a facile entry to organotin(IV) carboxylates

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ABSTRACT

A simple protocol is described for the oxidative transformation of aldehydes to the corresponding organotin(IV) carboxylates in high yields (up to 90%) that utilizes atmospheric O_2 as the sole oxidant, *N*-heterocyclic carbene as catalyst (at 10 mol %), and tributyl tin chloride as stannylating agent. The uniqueness of the reaction lies in the direct conversion of aldehydes to the corresponding organotin(IV) carboxylates via stannylation of carboxylic acids, generated from the reaction of a Breslow intermediate with O_2.

Organotin(IV) carboxylates have attracted considerable attention owing to the enormous variety of discrete or polymeric structural topologies[1] and their unexpected properties as potential pharmaceuticals such as anti-tumor,[2] antimicrobial,[3] anti-fungal[4], and cytotoxic activity.[5] They are also used as fungicides,[6] pesticides,[7] antifouling coating materials,[8] preservatives for wood,[9] acaricides[10], and homogeneous catalysts[11] in industry. In the literature, their synthesis has been reported from the corresponding carboxylic acids[12] and their salts.[13] However, these methods suffer from disadvantages such as harsh reaction conditions, metals as by-products and often giving low yields.

In recent years, many NHC-catalyzed reactions have been reported for C–C, C–N, and C–O bond-forming reactions.[14] In particular, the direct esterification of aldehydes was well-documented with alcohols as nucleophiles under different oxidative conditions.[15] However, these reactions employ both boronic acids[16] and alkyl halides[17] under aerobic conditions. Recently, we reported a useful preparative procedure for the oxidative esterification[18] of aldehydes under aerobic oxidative conditions with alcohols. Thus, it is of interest to explore NHC catalyzed oxidative metallation of aldehydes with metal halides as electrophiles. In this Letter, we wish to report a new efficient and practical method for the one-step conversion of aldehydes directly into the corresponding organotin(IV) carboxylates using *N*-heterocyclic carbenes as catalysts (Scheme 1).

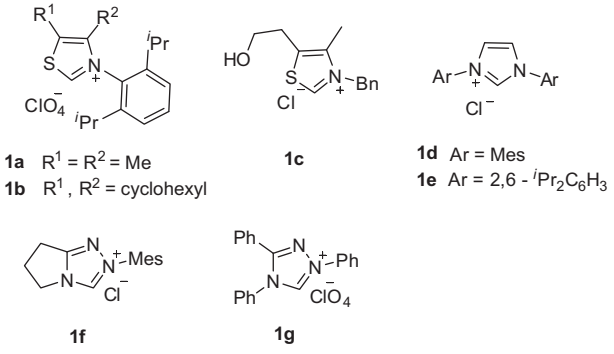
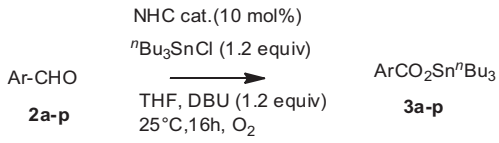


Figure 1. NHC precatalysts screened for oxidative stannylation.



Scheme 1. NHC-catalyzed oxidative stannylation of aromatic aldehydes.

Initially, we have chosen 4-nitrobenzaldehyde **2g** as a test substrate for the oxidative stannylation using tributyltin chloride (1.2 equiv) as tin source, NHC precatalyst **1a** (10 mol %), and DBU

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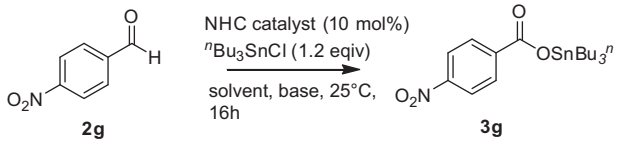
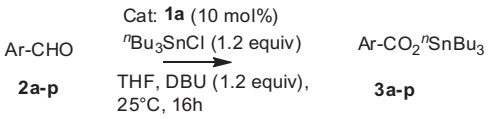
Table 1
Oxidative stannylaltion of 4-nitrobenzaldehyde: optimization studies[a]



Entry	Catalyst	Solvent	Base	Yield of **3g**[b] (%)
1	**1a**	CH_3CN	DBU	55
		THF	DBU	90
		DMF	DBU	35
		CH_2Cl_2	DBU	5
2	**1a**	THF	K_2CO_3	40
		THF	KO^{t}Bu	35
		THF	NaH	20
3	**1b**	THF	DBU	41
4	**1c**	THF	DBU	75
5	**1d**	THF	DBU	40
6	**1e**	THF	DBU	33
7	**1f**	THF	DBU	54
8	**1g**	THF	DBU	20

[a] Reaction conditions: 4-nitrobenzaldehyde (1 equiv), *n*-tributyltin chloride (1.2 equiv), NHC catalyst (10 mol %), base (1.2 equiv), under O_2 atmosphere; 25 °C, 16 h.
[b] Isolated yields after column chromatographic purification.

Table 2
Oxidative stannylaltion of aromatic aldehydes: substrate scope[a]



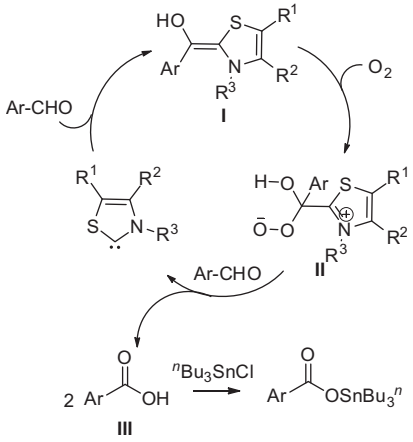
Entry	Substrate, Ar (**2a–p**)	Product (**3a–p**)	Yield[b] (%)
1	Benzaldehyde	**3a**	40
2	*m*-Tolualdehyde	**3b**	76
3	4-OMe-benzaldehyde	**3c**	79
4	3,4-(–OCH_2O–)benzaldehyde	**3d**	81
5	Salicylaldehyde	**3e**	74
6	3-NH_2-benzaldehyde	**3f**	71
7	4-NO_2-benzaldehyde	**3g**	90
8	2-NO_2-benzaldehyde	**3h**	85
9	4-Br-benzaldehyde	**3i**	70
10	4-CN-benzaldehyde	**3j**	87
11	3-Pyridine carboxaldehyde	**3k**	82
12	Furfural	**3l**	87
13	Cinnamaldehyde	**3m**	22 (84)[c]
14	4-Br-cinnamaldehyde	**3n**	79[c]
15	3,4-$(OMe)_2$-cinnamaldehyde	**3o**	72[c]
16	1-Br-3,4-dihydronaphthaldehyde	**3p**	74[c]

[a] Reaction conditions: aldehyde (5 mmol), *n*-tributyltin chloride (6 mmol), NHC catalyst **1a** (10 mol %), DBU (6 mmol), under O_2 atmosphere; 25 °C, 16 h.
[b] Isolated yield after column chromatographic purification.
[c] NHC catalyst **1d** was used.

(1.2 equiv) as base in CH_3CN, which produced tri-*n*-butyltin 4-nitrobenzoate **3g** in 55% yield (Table 1, entry 1). We conducted several experiments to improve the yield and found that THF was the best choice (90%) while other solvents (DMF, CH_2Cl_2) gave only moderate yield of **3g**. Use of other inorganic bases (K_2CO_3, KOBu,^{t} and NaH) resulted in a sluggish reaction with poor yields. DBU was thus chosen as the base for further optimization (Table 1, entry 2). Among the NHC precatalysts[18,20] screened (Fig. 1), thiazolium (**1b** and **1c**)-based precatalysts afforded **3g** in 41% and 75% yields, respectively while the imidazolium (**1d** and **1e**) and triazolium (**1f** and **1g**)-based precatalysts also gave only moderate yields (54%).

With the optimized conditions in hand, we examined the substrate scope of the reaction. Various aldehydes were then subjected to oxidative stannylation; the results of which are presented in Table 2. Aromatic aldehydes, having electron-withdrawing and releasing groups at various positions on the aromatic ring were reacted to give the corresponding organotin(IV) carboxylates (Table 2) in excellent yields. Also, heteroaromatic aldehydes underwent this oxidative stannylation efficiently to give the corresponding tin(IV) carboxylates in 82% and 87% yields, respectively. In the case of α,β-unsaturated aldehydes, the oxidative stannylation under the above optimized conditions gave **3m** (entry 13, Table 2) in low yield (22%). However, replacing **1a** with **1d** gave the corresponding α,β-unsaturated acid stannane in 84% yield. Thus, with **1d** as precatalyst, α,β-unsaturated aldehydes (entries 14–16) underwent this reaction successfully to give excellent yields of the corresponding organotin(IV) carboxylates. The structure of tri-*n*-butyltin carboxylates **3a–p** was specifically ascertained on the basis of spectroscopic techniques. Their carbonyl carbons have shown typical signals in the range δ 169–172 in their ^{13}C NMR spectra. Strong characteristic IR absorptions in the range 1600–1640 cm^{-1} for all the tri-*n*-butyltin carboxylates confirmed the presence of carboxylate functionality. Their structures were further supported by their high resolution mass spectra.

Based on literature reports,[17] a probable mechanistic pathway is shown in Scheme 2. The Breslow intermediate **I**, upon reaction with O_2 gives the peroxy anion **II**,[17a] which then reacts with another molecule of aldehyde to afford carboxylic acid in situ; the stannylation of which with tri-*n*-butyltin chloride produces tri-*n*-butyltin carboxylates.



Scheme 2. Proposed mechanistic pathway for tributyltin(IV) carboxylates.

In conclusion, we have developed an efficient catalytic process[19] for the preparation of organotin(IV) carboxylates[21,22] using *N*-heterocyclic carbene catalyzed oxidative metallation of aldehydes under aerobic conditions. This methodology illustrates the use of metal electrophiles in NHC catalyzed reactions.

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20. Typical experimental procedure: to a stirred solution of *N*-heterocyclic carbene precursor (10 mol %), DBU (6 mmol), and aldehyde (5 mmol) in anhydrous THF (5 ml), tri-*n*-butyltin chloride (6 mmol) was added under an O_2 atmosphere. The reaction mixture was then stirred at 25 °C for 16 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated, followed by the addition of H_2O (50 mL). It was extracted with EtOAc (3 × 50 ml) and the combined organic layers dried over anhydrous Na_2SO_4. Removal of solvent gave organotin carboxylates, which were purified by column chromatography over silica gel using pet ether/EtOAc (1/19) as eluent to obtain pure tri-*n*-butyltin(IV) carboxylates in high purity.
21. Tri-*n*-butyltin(IV) furan-2-carboxylate (**3l**): Yield: 87%, colorless liquid; IR ($CHCl_3$, cm^{-1}): 1011, 1364, 1389, 1409, 1549, 1579, 1600, 2853, 2921, 2954; ^1H NMR (200 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.11 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 3.3 Hz, J = 1.6 Hz, 1H), 1.85–1.58 (m, 6H), 1.48–1.25 (m, 12H), 0.92 (t, J = 7.1 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.2, 146.3, 145.3, 117.0, 111.5, 27.8, 27.0, 16.8 and 13.6; Analysis: $C_{17}H_{30}O_3Sn$ requires C, 50.90; H, 7.54. Found: C, 50.78; H, 7.39; MS (ESI): $[M+Na]^+$ calcd for $C_{17}H_{30}NaO_3Sn$: 425.11; found: 425.44.
22. Tri-*n*-butyltin(IV) 3,4-dimethoxy-*trans*-cinnamate (**3o**): Yield: 72%, colorless solid, mp: 224–225 °C; IR ($CDCl_3$, cm^{-1}); 2954, 2922, 1639, 1513, 1262, 1139, 1025. ^1H NMR (200 MHz, $CDCl_3$): δ 7.62 (d, J = 15.9 Hz, 1H), 7.07 (m, 2H), 6.83 (d, J = 8.6 Hz, 1H), 6.32 (d, J = 15.9 Hz, 1H), 3.90 (s, 6H), 1.83–1.62 (m, 6H), 1.36–1.28 (m, 12H), 0.93 (t, J = 7.2 Hz, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.3, 151.1, 149.2, 145.2, 127.5, 122.7, 110.9, 109.6, 55.8, 27.8, 27.0, 16.5 and 13.7; Analysis: $C_{23}H_{38}O_4Sn$ requires C, 55.55; H, 7.70. Found: C, 55.77; H, 7.48. MS (ESI): $[M+Na]^+$ calcd for $C_{23}H_{38}NaO_4Sn$: 521.16; found: 521.25.