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Palladium-Catalyzed Carbonylative Synthesis of Acylstannanes from Aryl Iodides and Hexamethyldistannane

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Dedicated to Professor Laszlo Kollar on the occasion of his 65th birthday!



ABSTRACT: In this communication, we describe a new method for the carbonylative synthesis of acylstannanes from aryl iodides and hexamethyldistannane. With $Pd(PPh_3)_4$ as the catalyst and toluene as the solvent at 60 °C under 10 bar CO for 16 h, the desired acylstannanes were obtained in good to excellent yields. In order to facilitate isolation and analysis, the obtained acylstannanes were transformed into the corresponding benzoic acids by simply stirring under air for 5 hours.

Keywords: Palladium catalyst; carbonylation; aryl iodides; acylstannane; cross-coupling

Recently, acylsilanes as versatile synthetic building blocks have been employed in various interesting transformations in organic synthesis.^[1] Since Brook and Corey independently reported the first example for the synthesis of acylsilanes,^[2,3] a number of methods for synthesis of acylsilanes have been developed.^[4,5] In 2012, a palladium-catalyzed carbonylative coupling of aryl iodides with TMS-TMS to give the corresponding Acyl-TMS was developed in Beller's group.^[5] However, their heavier congeners, acylgermanes and acylstannanes, group-14 element compounds, don't get much attention as acylsilanes, despite their theoretical and practical interest in organic synthesis. Recently, our group reported a carbonylative method for synthesis of acylgermanes. From the same strategy, we envisage the synthesis of acylstannanes through a carbonylative reaction. From literature, some methods have been developed for the preparation of acylstannanes (Scheme 1). In 1968, Peddle reported the first example for synthesis of acylstannanes by the addition of triphenyltinlithium to acyl chlorides at -70°C (Scheme 1a).^[7] Subsequently, Quintard and coworkers able to prepare acylstannanes from aldehydes and a Sn-Mg organometallic reagent (Scheme 1b).^[8] In addition, Hassner and co-workers developed a method for the preparation of acylstannanes by acidolysis of stannylated alkyl vinyl ethers (Scheme 1c).^[9] In 1983, Klumpp and co-workers obtained acylstannanes through hydrolysis of a 1,3-dioxane derivative (Scheme 1d).^[10] In 1990, Mitchell and co-workers got acylstannanes by reacting acyl chlorides with hexamethylditin in the presence of palladium catalysts (Scheme 1e).^[11] Additionally, Sander and co-workers described a method for the preparation of acylstannanes through photolysis of stannylfuranes (Scheme 1f.^[12]

Scheme 1. Methodologies for Acylstannanes Synthesis

a. Triphenyltinlikhium reacts with acyl chlorides

$$\begin{array}{c} & & \\ R \\ \hline \\ CI \end{array} + Ph_3SnLi \longrightarrow R \\ \hline \\ SnPh_3 \end{array}$$
b. Tributyltinmagnesium chloride reacts with aldehyde
Bu_SnMgCI + 2 RCHO $\longrightarrow R^{-C} \\ SnBu_3 \end{array} + RCH_2OMgCI$

c. Acidolysis of stannylated alkyl vinyl ethers

$$\underbrace{ \xrightarrow{\text{OMe}} 1. \text{ }^{\text{BuLi}}}_{2. \text{ Me}_3 \text{SnCl}} \underbrace{ \xrightarrow{\text{OMe}} H^{+}}_{\text{SnMe}_3} \underbrace{ \xrightarrow{\text{OMe}}}_{\text{SnMe}_3} \underbrace{ \xrightarrow{\text{$$

d. Hydrolysis of a 1,3-dioxane derivative

e. Palladium catalyzed coupling reaction

$$\begin{array}{c} O \\ R^1 \\ CI \end{array} + \begin{array}{c} R^2 \\ R^2 \\ R^2 \\ R^2 \end{array} \xrightarrow{[Pd]} O \\ R^1 \\ R^1 \\ R^2 \\ R^2 \end{array} \xrightarrow{[Pd]} O \\ R^1 \\ R^2 \\ R^2 \\ R^2 \\ R^2 = Me, Bu$$

f. Photolysis of stannylfuranes

TMS

$$\underbrace{Me_{3}Sn}_{H} \underbrace{O}_{H} \underbrace{N_{2}}_{H} \underbrace{435 \text{ nm}}_{H} \left[\underbrace{Me_{3}Sn}_{H} \underbrace{O}_{H}_{H} \right] \underbrace{Rearrangement}_{H} \underbrace{Me_{3}Sn}_{H} \underbrace{O}_{H}_{H} \underbrace{Me_{3}Sn}_{H} \underbrace{O}_{H}_{H} \underbrace{Me_{3}Sn}_{H} \underbrace{Me_{3}Sn}_{H} \underbrace{O}_{H}_{H} \underbrace{Me_{3}Sn}_{H} \underbrace{Me$$

g. This work Direct carbonylation of aryl iodide with hexamethyldistannane

$$R_{U}^{fi}$$
 + CO + Me₃Sn-SnMe₃ (Pd) R_{U}^{fi} SnMe

On the other hand, since Heck and co-workers reported the first example in 1970s, Pd-catalyzed coupling reaction of aryl halides with CO and different nucleophiles has been widely used not only in academia but also in industry for the preparation of the carbonyl-containing compounds.^[13] In 1985, in their studies on palladium-catalyzed synthesis of symmetrical ketones or diketones from aroyl chlorides and Et₆Sn₂, Bumagin and co-workers described one example on palladium-catalyzed synthesis of 4,4'-dimethoxybenzil (71% yield) from 4-iodoanisole (2 equiv) in the presence of Et₆Sn₂ under CO pressure (8 bar) at 111 °C.^[14] The authors proposed acylstannane as the intermediate, which is most likely the case, however, no detection of acylstannane was possible rather than diketone and ketone.

Based on our continual research interests in carbonylation chemistry, we report here a new method for the synthesis of acylstannanes by palladium-catalyzed carbonylation of aryl iodides with hexamethyldistannane.

The initial investigation was carried out with 1-iodo-4methoxybenzene and hexamethyldistannane as the substrates. To product delight, the desired (4 our methoxy)benzoyltrimethylstannane could be detected on GC-MS as the major product with Pd(PPh₃)₄ as the catalyst in THF at 80 °C for 16 hours under 10 bar CO. However, the acylstannane was sensitive to oxygen and light, we failed to isolate the acylstannanes by column chromatography. In order to obtain isolated yield and spectroscopic characterization, the acylstannane product was completely oxidized under air to give the corresponding benzoic acid. Then we screened parameters to establish the optimal conditions for this reaction (Table 1). In the screening of reaction temperature, we found that temperature was critical to the reaction, too high or too low temperature was not conducive to the improvement of yield and 60 \square was the best temperature for this reaction (Table 1, entries 1-5). Low reaction temperature leads to low conversion of substrates, while arylstannane becomes the main product under higher reaction temperature. Next, a set of solvents were tested, and the yield increased significantly to 92% when toluene was employed (Table 1, entry 6). 1,4-Dioxane and DCE gave moderate yields (Table 1, entries 7 and 8), no product was detected in MeCN (Table 1, entry 9). When we removed the palladium catalyst or changed the catalyst to Cu or Ni, this reaction could not proceed at all (Table 1, entries 10-12). It revealed the unique and important catalytic role of palladium in this carbonylative reaction. The target product can still be produced in 61% yield when we carried out the reaction under atmospheric pressure CO (Table 1, entry 13). Finally, we were delighted to find that the catalyst loading can be decreased to 1 mol% while gave a similar yield 91% (Table 1, entry 14). In order to compare with Bumagin's system, 2 equiv of 4-iodoanisole was added under our standard condition and 4,4'-dimethoxybenzil become the main product even under lower reaction temperature. Hence, the product selectivity between arylstannane and ketone is mainly controlled by the loading aryl iodides added.

Table 1. Optimization of the Reac	tion Conditions.
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MeC		► Me ₃ Sn−SnMe ₃ 1)[F 2) u	^p d] Inder air, 5 h M	е0 ОН
	1a	2		3a
entry	catalyst	solvent	temp	yield (%)
1	$Pd(PPh_3)_4$	THF	r.t.	trace
2	$Pd(PPh_3)_4$	THF	40 🗆	5

3	Pd(PPh ₃) ₄	THF	60 🗆	66
4	Pd(PPh ₃) ₄	THF	80 🗆	34
5	Pd(PPh ₃) ₄	THF	100 🗆	7
6	Pd(PPh ₃) ₄	Toluene	60 🗆	92(83) ^b
7	Pd(PPh ₃) ₄	1,4-	60 🗆	68
8	Pd(PPh ₃) ₄	Dioxane DCE	60 🗆	57
9	Pd(PPh ₃) ₄	MeCN	60 🗆	0
10	-	Toluene	60 🗆	0
11	CuI/Bipyridine	Toluene	60 🗆	0
12	NiBr ₂ /Bipyridine	Toluene	60 🗆	0
13 ^c	Pd(PPh ₃) ₄	Toluene	60 🗆	61
14^d	Pd(PPh ₃) ₄	Toluene	60 🗆	91

^aReaction conditions: **1a** (0.2 mmol), **2** (0.22 mmol), catalyst (2 mol %), solvent (0.5 mL), 10 bar CO, 16 h, then stirring under air 5 h, NMR yield. ^bisolated yield. ^{c1} bar CO. ^d catalyst (1 mol %)

With the optimal reaction conditions in hand, we then tested other aryl iodides in this carbonylative reaction (Table 2). First, we tried iodobenzene as the starting material, the expected benzoic acid was obtained with 71% yield under the standard conditions (3b). As shown in Table 2, iodobenzenes with methyl-substituted at different positions could be well tolerated and delivered the target products in good to excellent yields (3c-3f). When the substituents were replaced with ethyl and tert-butyl, the corresponding products were achieved with 64% and 83% yields, respectively (3g, 3h). Moreover, the reaction with 1iodonaphthalene proceeded smoothly as well and gave the desired product in 87% yield (3i). Gratifyingly, N-pyrrole-substituted iodobenzene was also well tolerated in this transformation, delivering the corresponding benzoic acid in 54% yield (3j). When the methoxy group located in the meta-position, the yield was lower than in the para-position (3k). As the number of substituted methoxy groups increased, the yield of the corresponding product increased (31). Unfortunately, substrates with electron-withdrawing groups, such as -C1, -F, $-CF_3$, -COOMe, lead to low yields of the target products (< 10%; see Support Information). One of the main reasons was that the acylstannanes from electronwithdrawing substituted aryl iodides are easily to go to decarbonylation to give ArSnMe₃ even under low pressure of carbon monoxide. ArSnMe₃ were detected in these cases. Additionally, (Bu₃Sn)₂ and (Et₃Sn)₂ were tested with 1-iodo-4-methoxybenzene under our standard conditions as well, but no desired products could be detected. It is also important to mention that a control experiment without hexamethyldistannane was carried out as well. Only trace amount of the corresponding carboxylic acid was detected in GC-MS which might due to the trace amount of water in the solvent and produced via hydroxycarbonylation.

Based on our results and literature,^[15-20] a plausible reaction pathway is proposed in Scheme 2. First, oxidative addition of palladium to aryl iodide to obtain arylpalladium complex **A**. Next, acylpalladium complex **B** is generated by the migratory insertion of carbon monoxide. Subsequently, intermediate **B** undergoes transmetalation with distannane to give stannyl complex **C**, and the by-product ISnMe₃ can be detected on GC-MS. The final acylstannane products can be delivered by reductive elimination from complex **C**, and meanwhile regenerate the active palladium species for the next catalytic cycle.

Table 2. Synthesis of Acylstannanes from Aryl Iodides. Reaction scale: 0.50 mmol, isolated yields.

R ^{fi} U 1a 1 equiv	+ CO + Me ₃ Sn-SnMe ₃ 10 bar 2 1.1 equiv	Pd(PPh ₃)₄ (1 mol %) PhMe (1 mL) 60 ℃, 16 h then under air, 5 h	
Entry	Aryl iodides	Products	Yield
1	MeO	мео	3a 82%
2		Соон	3b 71%
3		Соон	3c 78%
4		Соон	3d 64%
5		СООН	3e 82%
6		СООН	3f 88%
7		Соон	3g 64%
8		Соон	3h 83%
9		СООН	3i 87%
10		CN-CCOOH	3j 54%
11	OMe	Соон	3k 63%
12	MeO MeO OMe	MeO MeO OMe	3 81%

Scheme 2. Proposed Reaction Mechanism



In conclusion, an interesting procedure for the synthesis of acylstannanes from aryl iodides and hexamethyldistannane by direct carbonylation has been developed.^[16-20] With Pd(PPh₃)₄ as the catalyst and toluene as the solvent at 60 \Box under 10 bar CO for 16 h, the desired acylstannanes were obtained in good to excellent yields which can be easily converted into the corresponding benzoic acids by simply stirring under air.

Notes

The authors declare no competing financial interests.

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proposition

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	+ CO + Me ₃ Sn-SnMe ₃	Pd(PPh ₃) ₄ (1 mol %)	
1a 1 equiv	10 bar 21.1 equiv	then under air, 5 h	3
Entry	Aryl iodides	Products	Yield
1	MeO	МеО	3a 82%
2		СООН	3b 71%
3		СООН	3c 78%
4		СООН	3d 64%
5		СООН	3e 82%
6		СООН	3f 88%
7		СООН	3g 64%
8		СООН	3h 83%
9		СООН	3i 87%
10		CN COOH	3j 54%
11	OMe	СООН	3k 63%
12	MeO MeO OMe	MeO MeO OMe	3i 81%

° ° 1. The first palladium catalyzed carbonylative synthesis of acylstannanes from aryl iodides and hexamethyldistannane has been developed.

2. With $Pd(PPh_3)_4$ as the catalyst at 60 °C, the desired acylstannanes were obtained in good to excellent yields.

3. The obtained acylstannanes can be transformed into the corresponding benzoic acids by simply stirring under air.

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We have no conflict of interest to declaration!

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