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LETTERS

SYNTHESIS OF ARYL AND ALKYL ACYLSILANES USING TRIMETHYL(TRIBUTYLSTANNYL)SILANE

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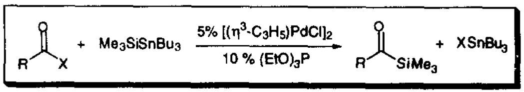
Abstract Palladium catalyzed coupling of acid chlorides and trimethyl(tributylstannyl)silane proves to be a convenient method for the preparation of both aromatic and aliphatic acylsilanes.

Keywords: *palladium compounds, silicon compounds, tin compounds.*

Acylsilanes are well known for both their interesting spectroscopic behavior and considerable synthetic utility.[1] These compounds have served as building blocks for heterocycle synthesis,[1a] proven useful as electrophiles in diastereoselective addition reactions,[1] and can be viewed as acyl anion precursors.[1] Given the chemical versatility of acylsilanes, many elegant methods have been developed to synthesize these compounds, with most routes falling into the electrophilic[1,2] or nucleophilic[1,3] silylation categories. While some of these methods have proven quite useful over the years, their reliance on either strong bases, low temperatures, multi-step protocols, or lack of generality have provided the impetus for continued research in this area.

In response to some of these problems, Yamamoto[4] has described a very convenient and mild synthesis of acylsilanes involving the palladium catalyzed coupling of benzoyl chlorides with hexamethyldisilane ($Me_3SiSiMe_3$) to afford *aromatic* acylsilanes in yields ranging from 37-81%. Unfortunately, this method lacks generality in that it fails during the preparation of *aliphatic* acylsilanes.[5] In need of several aliphatic acylsilanes, we surveyed many of the existing procedures, before deciding to explore the possibility of modifying Yamamoto's method so as to allow the synthesis of these compounds. In this Letter, we wish to report the successful outcome of this investigation.

Table I



Entry	R	X	Temp (°C)	Time	Yield (%)
1	*n*-C_4H_9	Cl	110	20 min	63
2	*n*-C_7H_{25}	Cl	rt	15 days	43
3	*n*-C_7H_{25}	Cl	110	16 hr	74
4	$C_4H_9(Et)CH$	Cl	75	10 hr	45[a]
5	cyclo-C_6H_{11}	Cl	75	12 hr	56[a]
6	Ph	Cl	110	20 min	66
7	Ph	$PhCO_2$	110	20 min	18
8	Ph	Cl	75	1.7 hr	57[a]
9	*o*-ClPh	Cl	110	20 min	30
10	*p*-MeOPh	Cl	110	20 min	35

[a] reactions were carried out under a CO atmosphere

Aware that the polarized and weaker Si—Sn bond of the commercially available[6] trimethyl(tributylstannyl)-silane ($Me_3SiSnBu_3$) make this reagent more reactive than the disilane,[7] we decided to study its employment in the construction of both aromatic and aliphatic acylsilanes. Thus a solvent-free mixture of benzoyl chloride and $Me_3SiSnBu_3$ together with catalytic amounts $(EtO)_3P$ and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ were reacted at 110 °C. Although, reaction of the corresponding disilane under the same conditions required between 5 to 24 hour reaction times,[4a] we were surprised to see our pale yellow solution turned black after 10 min, suggesting a successful coupling. Indeed, workup of the reaction after 20 min reaction time afforded the desired benzoyltrimethylsilane in 66% yield (Table I, entry 6)[8] which compared quite favorably to Yamamoto's yield of 69%. We next moved to the aliphatic

0040-4039/99/$ - see front matter
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series, where we were even more pleased to see that our hypothesis had proven correct. Subjecting valeryl chloride (entry 1) to the same conditions for 20 min gave valeryl trimethylsilane[8] in a satisfying 63% yield. During our examination of other aliphatic acid chlorides longer reaction times were occasionally employed (entry 3). We also explored the option of running these reactions at lower temperatures (entries 2, 4, 5, and 8). Again longer reaction times were required, but even at 25 °C octanoyltrimethylsilane[5a,8] could be prepared in fair yield, whereas this reaction with $Me_3SiSiMe_3$ failed at temperatures below 70 °C.[4a] In practice though, we found the couplings were best run at 75 °C or above. Additionally, we observed modest improvements in our yields when the reactions were carried out under a CO atmosphere (1 atm).[5b]

While this method clearly appears to be general for the construction of both aromatic and aliphatic acylsilanes, several additional points are worth noting. Like Yamamoto, we observed a diminution of yields when the electronics of the aryl system are perturbed (entries 9 and 10). Furthermore, this method does suffer from competing formation (29% in entry 8) of the acylstannanes. Fortunately, the unstable acylstannanes[9] can be easily separated from the desired acylsilane and recycled back to starting material via hydrolysis and acid chloride formation. Finally, we were able to expand the method to include the employment of acid anhydrides (entry 7), albeit with low efficiency.

Representative procedure: di-μ-chloro-bis(η^3-allyl)dipalladium (II) (14 mg, 77 μmol) was placed into a 5 mL round bottom flask which was charged with CO (1 atm) and protected from light. Triethyl phosphite (27 μl, 155 μmol) and trimethyl(tributylstannyl)silane (0.63 mL, 1.8 mmol) were added via syringe and the mixture was allowed to stir at rt for 3 min. Cyclohexanecarbonyl chloride (0.2 mL, 1.5 mmol) was then added and that mixture was heated to 75 °C. After 12 hr palladium metal precipitate was observed. The reaction was cooled and then transferred onto a foil wrapped silica gel column. Elution with 3% diethylether in pentane gave 154 mg (56%) of the acylsilane as a pale yellow liquid.

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