



Pergamon

Tetrahedron Letters 40 (1999) 3113-3114

TETRAHEDRON
LETTERSSYNTHESIS OF ARYL AND ALKYL ACYLSILANES USING
TRIMETHYL(TRIBUTYLSTANNYL)SILANE

Feng Geng and Robert E. Maleczka, Jr.*

Department of Chemistry, Michigan State University, East Lansing, MI, 48824, U.S.A.

Received 5 February 1999; revised 22 February 1999; accepted 24 February 1999

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. © 1999 Elsevier Science Ltd. All rights reserved.**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, Yamamoto⁴ has described a very convenient and mild synthesis of acylsilanes involving the palladium catalyzed coupling of benzoyl chlorides with hexamethyldisilane ($\text{Me}_3\text{SiSiMe}_3$) 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.

Aware that the polarized and weaker Si—Sn bond of the commercially available⁶ trimethyl(tributylstannyl)silane ($\text{Me}_3\text{SiSnBu}_3$) 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 $\text{Me}_3\text{SiSnBu}_3$ together with catalytic amounts $(\text{EtO})_3\text{P}$ and $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ 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

Table I

Entry	R	X	Temp (°C)	Time	Yield (%)
1	<i>n</i> -C ₄ H ₉	Cl	110	20 min	63
2	<i>n</i> -C ₇ H ₁₅	Cl	rt	15 days	43
3	<i>n</i> -C ₇ H ₁₅	Cl	110	16 hr	74
4	C ₄ H ₉ (Et)CH	Cl	75	10 hr	45 ^a
5	cyclo-C ₆ H 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	<i>o</i> -ClPh	Cl	110	20 min	30
10	<i>p</i> -MeOPh	Cl	110	20 min	35

^areactions were carried out under a CO atmosphere

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 trimethylsilane⁸ 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 Me₃SiSiMe₃ 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 acylstannanes⁹ 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 μ mol) was placed into a 5 mL round bottom flask which was charged with CO (1 atm) and protected from light. Triethyl phosphite (27 μ l, 155 μ mol) 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.

Acknowledgments. This investigation was generously supported by the NIH (HL-58114) and Michigan State University (start-up funds for R.E.M.).

REFERENCES AND NOTES

- For reviews see: (a) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *J. Organometal. Chem.* **1998**, *567*, 181-189. (b) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147-195. (c) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647-660.
- For methods involving the use of acyl anion equivalents see: (a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431-434. (b) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434-436. (c) Yoshida, J.; Matsunaga, S.; Ishichi, Y.; Maekawa, T.; Isoe, S. *J. Org. Chem.* **1991**, *56*, 1307-1309. (d) Katritzky, A. R.; Wang, Z.; Lang, H. *Organometallics* **1996**, *15*, 486-490 and cited references.
- For the use of *tris*-trimethylsilylaluminum see: (a) Kang, J.; Lee, J. H.; Kim, K. S.; Jeong, J. U.; Pyun, C. *Tetrahedron Lett.* **1987**, *28*, 3261-3262. For the use of silylcuprates see: (b) Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Ricci, A. *J. Org. Chem.* **1988**, *53*, 3612-3614. (c) Bonini, B. F.; Comes-Franchini, M.; Mazzanti, G.; Passamonti, U.; Ricci, A.; Zani, P. *Synthesis* **1995**, 92-96. (d) for an efficient approach to TIPS acylsilanes see: Lipshutz, B. H.; Lindsley, C.; Susfalk, R.; Gross, T. *Tetrahedron Lett.* **1994**, *35*, 8999-9002.
- (a) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 1653-1656. (b) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974-979.
- (a) Yamamoto prepared octanoyltrimethylsilane in 18% yield with concomitant formation of several unidentified products (Ref. 4a). (b) see Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886-5893 for related discussions.
- (a) Aldrich Chemical Co. (b) For a preparation see Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561-3566. (c) We adapted a procedure by Ritter, K. *Synthesis* **1989**, 218-221 to synthesize Me₃SiSnBu₃.
- Kosugi, M.; Ohya, T.; Migata, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3539-3540.
- All synthetic compounds were purified by flash chromatography on silica gel. The structure assigned to each compound is in accord with its infrared, 300-MHz ¹H NMR and 75-MHz ¹³C NMR spectra, as well as appropriate parent ion identification by high resolution mass spectrometry.
- Peddle, G. J. D. *J. Organometal. Chem.* **1968**, *14*, 139-147.