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PREPARATION OF SUBSTITUTED BENZOYLTRIMETHYLSILANES BY THE PALLADIUM-CATALYZED SILYLATION OF SUBSTITUTED BENZOYL CHLORIDES WITH HEXAMETHYLDISILANE

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Summary: A direct preparative route to benzoyltrimethylsilane has been found by the reaction of benzoyl chloride with hexamethyldisilane in the presence of a specified palladium(II) complex as catalyst.

We previously reported the group VIII metal complex-catalyzed reactions of pentamethyldisilane or vinylpentamethyldisilane which involved a facile cleavage of the silicon-silicon bond.[1] Similar reaction with *sym*-tetramethyldisilane is very useful for the generation of a formally divalent dimethylsilylene which is effectively transferred to an added acetylene compound to form a novel 1-silacyclopentadiene framework.[2]

Hexamethyldisilane has also been found to undergo the Si-Si bond scission in the presence of Pd(II) complexes under forced conditions. Thus, Sakurai and collaborators have reported the electron donor properties of the Si-Si bond and disclosed a novel silylation reaction of activated acetylenes or olefins using certain disilane derivatives in the presence of Pd(II) complexes.[3] On the other hand, Matsumoto, Nagai, and coworkers have found that tetrakis(triphenylphosphine) palladium(0) catalyzes the silylation of aryl halides, allyl halides or vinyl halides with disilane compounds such as $Cl_nMe_{6-n}Si_2$ (n = 0, 2, and 4).[4] The relative reactivity of the disilanes appears to indicate that the electron acceptor properties of the Si-Si linkage facilitate the silylation reactions.

Taking advantage of the reactivity of these disilane compounds, we have now found that a direct silylaiton of benzoyl chloride with hexamethyldisilane does take place by using di-μ-chloro-bis(η^3-allyl)dipalladium(II), $[(\eta^3\text{-}C_3H_5)PdCl]_2$, plus specified ligands as catalyst (eq. 1).

Although the Pd(II) complex was not a sole choice, the ligand employed was found to play a decisive role for the successful catalytic reaction.

$$PhCOCl + Me_3SiSiMe_3 \xrightarrow[2L,\quad 110^\circ C]{1/2[(\eta^3\text{-}C_3H_5)PdCl]_2} PhCOSiMe_3 + ClSiMe_3 \qquad (1)$$

The following procedure for the preparation of benzoyltrimethylsilane is typical: $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (27.4 mg, 0.15 mmol) and triethyl phosphite (49.8 mg, 0.30 mmol) were placed in a thick glass tube with a screw cap under argon. Hexamethyldisilane (0.64 ml, 3.2 mmol) was added and the mixture was stirred for 5 min at room temperature. Benzoyl chloride (0.35 ml, 3.0 mmol) was then added and the reaction mixture was heated at 110°C with stirring. The progress of the reaction was conveniently monitored by GLC analysis.

After the reaction was completed, the mixture was cooled and distilled directly under reduced pressure. Further purification of the yellow benzoyltrimethylsilane (1a), if necessary, was carried out by a column chromatography. A small amount of trimethylphenylsilane (2) was always found as a by-product, the ratio of 1a to 2 being 96 : 4.

Use of triphenylphosphine, diphenylphosphinous chloride, phenylphosphonous dichloride, or triphenyl phosphite as a ligand resulted in either lowering the conversion of the reaction or diminishing the ratio of 1a to 2 considerably (*ca* 1 : 1). The reaction did not take place at all at 70°C. In addition, no solvent was advantageous for the reaction. Use of toluene as solvent (0.5, 1.0 or 2.0 ml/mmol of benzoyl chloride) simply caused the reaction to be retarded.

Substituted benzoyl chlorides were also silylated by the procedure described above to give the corresponding substituted benzoyltrimethylsilanes (1b-g) with fair to moderate yields. The results are summarized in the Table.

There have been several means of the preparation of a variety of acyltrimethylsilanes.[5] Some of the procedures which seem to be of wide applicability employ the reductive metalation of appropriate aliphatic[5c,d] or aromatic carboxylic acid esters,[5f] followed by treatment with chlorotrimethylsilane and in turn selective hydrolysis to regenerate an acyl functionality.

Although there remains an ambiguity as to the catalytic behavior,[6] the Table clearly shows that the present reaction provides a direct and the simplest preparative route to substituted benzoyltrimethylsilanes. It deserves to be mentioned that four substituted benzoyltrimethylsilanes (1d-g) with electronegative substituents are all newly prepared.[7] These substituents otherwise very sensitive to reducing conditions are intact during the present procedure.

Finally, the fact that trimethyl-*p*-nitrophenylsilane was found in a comparable yield with that of trimethyl-*p*-nitrobenzoylsilane (1g) indicates a facile decarbonylation from acyl-palladium intermediates which are often stable under more forced conditions.[8]

Attempted silylation of aliphatic acid chlorides afforded the desired acyltrimethylsilane in low yield with concomitant formation of several unidentified materials. Octanoyltrimethylsilane (3),[9] for example, was obtained in 18% yield.

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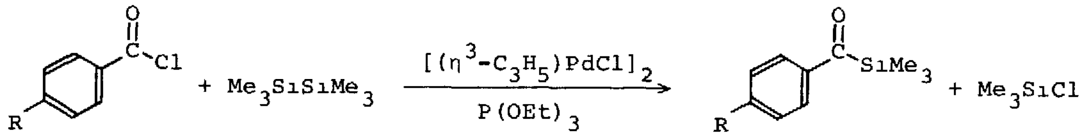
Table Preparation of Substituted Benzoyltrimethylsilanes (**1**)



(**1a**-**g**)

Entry	R	Pd Complex (mol%)	Phosphite (mol%)	Conditions[a] Temp (°C)	Time (h)	Yield[b] (%)	Lit
a	H	5	10	110	24	78[c]	5b, 5f
	H	5	10	110	24[d]	42	
	H	5	5	110	5.5	69	
b	Me	5	10	110	4.8	81	5f
	Me	5	5	110	5.5	73	
c	OMe	5	10	110	1.8	48	this work
d	Cl	5	10	110	17.5	71	this work
e	Br	5	10	110	5	48	this work
f	CO_2Me	5	10	110	3	47	this work
g	NO_2	5	10	110	1.8	37[e]	this work

a) GLC analysis, 96-100% conversion attained.
b) Isolated by distillation.
c) Trimethylphenylsilane (3%) as byproduct.
d) Toluene (0.5 ml) added as solvent.
e) Trimethyl-p-nitrophenylsilane (28%) isolated as byproduct.

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6) The π-allylpalladium(II) complex reacts readily with hexamethyldisilane to precipitate metallic palladium. It should be mentioned that triethyl phosphite reacts with benzoyl chloride in the manner of Arbuzov reaction in the absence of Pd(II) complex. Nevertheless, the use of triethyl phosphite as ligand of the Pd(II) catalyst is essential for the present reaction.

7) All new compounds gave satisfactory spectral data.

1c: NMR ($CDCl_3$, TMS) δ 0.33 (s, 9H, $\underline{Me}_3Si$), 3.82 (s, 3H, $O\underline{Me}$), 6.94 and 7.84 ppm (a pair of d, AA'BB', J = 8.4 Hz, aromatic 4H). IR (neat) 1615 cm^{-1} ($\nu_{C=O}$).

1d: NMR ($CDCl_3$, TMS) δ 0.35 (s, 9H), 7.30 and 7.62 (a pair of d, J = 8 Hz, aromatic 4H). IR (neat) 1615 cm^{-1}.

1e: NMR ($CDCl_3$, TMS) δ 0.37 (s, 9H) and 7.59 (br s, 4H). IR (neat) 1615 cm^{-1}.

1f: NMR ($CDCl_3$, TMS) δ 0.38 (s, 9H), 3.89 (s, 3H, $CO_2\underline{Me}$), 7.79 and 8.07 (a pair of d, J = 8.4 Hz, aromatic 4H). IR ($CDCl_3$) 1615 cm^{-1}.

1g: NMR ($CDCl_3$, TMS) δ 0.40 (s, 9H), 7.89 and 8.26 (a pair of d, J = 8.4 Hz, aromatic 4H). IR ($CDCl_3$) 1620 cm^{-1}.

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9) **3**: NMR (CCl_4, TMS) δ 0.16 (s, 9H), 0.89 (t, 3H, $\underline{Me}$), 1.26 (centered, 10H, $(C\underline{H}_2)_5$), and 2.48 (t, 2H, $COC\underline{H}_2$). IR (neat) 1620 cm^{-1}.

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