Organometallics 1987, 6, 974–979

Preparation of Substituted Benzoyltrimethylsilanes and -germanes by the Reaction of Benzoyl Chlorides with Hexamethyldisilane or -digermane in the Presence of Palladium Complexes as Catalysts

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Received September 2, 1986

Benzoyltrimethylsilanes are prepared in moderate to good yields (24–81%) from the novel reaction of hexamethyldisilane with benzoyl chlorides, catalyzed by dichloro(η^3-allyl)dipalladium(II) (1) and triethyl phosphite. The reaction tolerates a wide variety of meta and para substituents on the phenyl ring. Hexamethyldigermane and several bimetallic silicon–germaniums were also used in the reaction; the relative rates of group transfer from competitive benzoylation reactions are $PhMe_2Ge > Me_3Ge > PhMe_2Si > Me_3Si$. Ortho-substituted benzoyl chlorides and aliphatic acid chlorides gave lower yields of the corresponding acyltrimethylsilanes under the same reaction conditions.

Since the first preparation of an acylsilane (α-ketosilane) by Brook[1] some 30 years ago, a large number of acylsilanes have been prepared by a variety of reactions, constituting an interesting class of organosilicon compounds in both chemical and spectroscopic properties.[2a,b]

Representative methods of the preparation of acylsilanes hitherfore reported are (i) oxidation of α,α-dibromobenzylsilanes,[1] (ii) silylation of an acyl anion equivalent based on dithiane compounds followed by hydrolysis,[3a–d] (iii) reductive silylation of carboxylic acid esters,[4a,b] (iv) silylation (also applicable to germanium or tin compounds) of metalated enol ethers,[5] and (v) direct carbonylation–silylation of alkyllithiums.[6]

However, these reactions involve either strongly reducing conditions or oxidation procedures, suffering from strict limitations for preparing certain aroylsilane compounds that contain an electron-withdrawing substituent such as a nitro or an alkoxycarbonyl group. In fact, Brook et al.[7] have prepared six para-substituted benzoyltriphenylsilanes by way of substituted α,α-dibromobenzyltriphenylsilanes, and the preparation of the p-nitro derivative required laborious procedures.

Recently, palladium complex catalyzed reactions of disilane compounds with allylic halides,[8] aryl halides,[9] benzyl halides,[10] and α-halo ketones[11] to form the corresponding organosilanes have received considerable attention; an impetus of transmetalation of an organohalopalladium(II)–phosphine complex with hexamethyldisilane, for example, seems to play a key role in the catalytic reactions.

We have previously found a reaction of benzoyl chloride with hexamethyldisilane that is effectively catalyzed by dichlorobis(η^3-allyl)dipalladium(II) (1) with added triethyl phosphite to give benzoyltrimethylsilane in good yield (eq 1).

$$PhCOCl + Me_3SiSiMe_3 \xrightarrow[2P(OEt)_3,\ 110\,°C]{{}^1/_2[(\eta^3\text{-}C_3H_5)PdCl]_2} PhCOSiMe_3 + ClSiMe_3 \qquad (1)$$

The reaction was found to be applicable to a variety of ortho-, meta-, and para-substituted benzoyl chlorides as well.[12]

We report here the scope and limitations of the novel palladium-catalyzed acylation of hexamethyldisilane and of a series of bimetallic silicon–germanium compounds as well as hexamethyldigermane.

Substituent effect on the ultraviolet spectra of 23 meta- and para-substituted benzoyltrimethylsilanes thus newly prepared will be discussed in a following paper.

Results and Discussion

Preparation of Benzoylsilanes and -germanes Catalyzed by Palladium Complexes. (a) Palladium Catalyst. Reaction of benzoyl chloride with hexamethyldisilane proceeded smoothly in the presence of a π-allylpalladium complex **1** (5 mol %) and triethyl phosphite (10 mol %) as a supporting ligand in toluene or without solvent under an inert atmosphere at relatively elevated temperature (see eq 1). Tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, which is commonly used as a catalyst precursor for disilane reactions mentioned above,[8–11] was much less effective for this particular reaction.

Since the reaction of allyl chloride with hexamethyldisilane catalyzed by $Pd(PPh_3)_4$[8] likely involves a π-allyl–Pd(II)–phosphine species in the catalyst cycle, several phosphorus compounds were examined as a supporting ligand for **1** with respect to the palladium-catalyzed benzoylation of hexamethyldisilane in toluene. Reaction

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0276-7333/87/2306-0974$01.50/0

Table I. Ligand Effect on the Palladium-Catalyzed Benzoylation of Hexamethyldisilane

$$\mathrm{PhCOCl} + \mathrm{Me_3SiSiMe_3} \xrightarrow[\text{toluene}]{[\mathrm{Pd}] + \mathrm{L}} \underset{\mathrm{A}}{\mathrm{PhCOSiMe_3}} + \underset{\mathrm{B}}{\mathrm{PhSiMe_3}}$$

entry	[Pd] complex (mol %)	ligand (mol %)	temp, °C	time, h	convn,[a] %	A/B ratio
1	$Pd(PPh_3)_4$ (5)		110	12	4.6	
2	$[(\eta^3\text{-}C_3H_5)PdCl]_2$ (1) (5)		80	14	0[b]	
3	1 (10)	PPh_3 (20)	110	96	87	42/58
4	1 (5)	PPh_3 (10), $SnCl_2$ (5)	90	85	54	86/14
5	1 (5)	$P(OEt)_3$ (10)	90	65	71	93/7
6	1 (5)	$P(OEt)_3$ (10)	110	14	93[c]	96/4
7	1 (5)	$P(OPh)_3$ (10)	110	14	86	48/52
8	1 (5)	C[d] (10)	110	14	29	37/63
9	$Pd(OAc)_2$ (5)	$P(OEt)_3$	110	19	74	
10	$[P(OMe)_3]_2PdCl_2$ (5)		110	22	77	83/17

[a] Determined by GLC using pentadecane as an internal standard. [b] A palladium mirror was formed. [c] Isolated yield was 51%. [d] C is 1-phospha-2,6,7-trioxa-4-ethylbicyclo[2.2.2]octane.

temperature must be kept at 90 °C or above for appreciable reaction to occur. The results are summarized in Table I.

It was found that the product always was accompanied by a little decarbonylation product, trimethylphenylsilane, and that the conversion of benzoyl chloride and the ratio of $PhCOSiMe_3/PhSiMe_3$ (A/B in Table I) remarkably depended on the phosphines used. Thus, added triphenylphosphine, triphenyl phosphite, and a cage-like phosphite (C) were found to cause remarkable decarbonylation (entries 3, 7 and 8). A combination of PPh_3–$SnCl_2$ or trimethyl phosphite improved the ratio of A/B at the expense of the conversion (entries 4 and 10).

Triethyl phosphite (entries 5 and 6) is evidently the only satisfactory ligand for benzoylation, though the reason for effectiveness is not necessarily clear (vide infra). Recently, Eaborn et al.[13] have reported that $Pd(PPh_3)_4$ is an effective catalyst for the present reaction at higher reaction temperatures.

We have also examined the solvent effect (heptane, toluene, THF, 1,2-dichloroethane, and HMPA; 0.7 mL/mmol of substrate) on the conversion and selectivity in benzoyltrimethylsilane formation, and all but toluene retarded the reaction. As a result, reaction conditions given in entry 6, Table I, were found to be most satisfactory for the preparation of benzoyltrimethylsilane. Furthermore, the reactions can conveniently be carried out without toluene when the acid chloride used is soluble in hexamethyldisilane. The completion of the reaction is usually detected by deposition of the palladium mirror and a clear yellow solution persists.

(b) Acid Halides. For a qualitative comparison of the reactivities of benzoyl bromide, chloride, and fluoride, the extent of the reaction was monitored by GLC in terms of the yield of benzoyltrimethylsilane at a given reaction time under the same conditions as in entry 6, Table I, pentadecane being added as an internal standard. The yields for 4 h at 110 °C were found to be 43, 20, and 0% for benzoyl bromide, chloride, and fluoride, respectively.

Although high reactivity of benzoyl bromide is evident in the palladium-catalyzed benzoylation of hexamethyldisilane, ready availability of substituted benzoyl chlorides may still be the factor of choice.

Thus, a large number of ortho-, meta-, and para-substituted benzoyl chlorides were successfully used for the preparation of substituted benzoyltrimethylsilanes, most of which were newly obtained in modest to good yields. The reaction provides a novel preparative route to benzoylsilanes such as those in which the aroyl group carries an electron-withdrawing substituent (e.g., CO_2Me, CN, NO_2) that is hard to survive under reducing conditions. The commonly yellow products were readily purified by column chromatographic separation (silica gel, hexane–ether) followed by either short-path distillation for an oil or by recrystallization of a solid. In Table II are given the yields, melting points, and IR, ^1H NMR, and analytical data of ortho-, meta-, and para-substituted benzoyltrimethylsilanes, respectively.

$^{13}C\{^1H\}$ NMR data of meta- and para-substituted benzoyltrimethylsilanes are listed in Table III. Complete assignment of the observed chemical shifts of ring carbons could cleanly be made on the basis of those calculated by additive substituent effects (shift differences) of disubstituted benzene derivatives, 128.5 ppm being taken as a standard for the chemical shift of benzene.[14] Agreement between observed chemical shifts and calculated ones is excellent (within ±1.5 ppm) except for *m*-methoxycarbonyl (C3, 135.2 (130.4)), *m*-methoxy (C2, 110.4 (113.1)), and *p*-nitro derivatives (C1, 144.9 (147.2); C4, 149.9 (152.6)).

Since the chemical shift differences are small and sensitive to the concentration of samples, no significant correlation of substituent effects on either an ipso (bearing $COSiMe_3$) or a carbonyl carbon can be observed. Ultraviolet spectral data of meta- and para-substituted benzoyltrimethylsilanes will be discussed in a following paper.

As seen from Table II, palladium-catalyzed benzoylation of hexamethyldisilane using certain benzoyl chloride that bears an electron-withdrawing substituent on an ortho or a para position was found to undergo decarbonylation to give the corresponding substituted trimethylphenylsilane as a byproduct, resulting in exclusive decarbonylation in two cases (*o*-CO_2Me and *o*-NO_2). Usually palladium-catalyzed decarbonylation of acyl halides is known to proceed at 200 °C or above.[15]

It is worthy of note that the palladium-catalyzed reaction of phenylglyoxalyl chloride with hexamethyldisilane gave benzoyltrimethylsilane as the sole product in 52% yield, indicating a facile decarbonylation of the phenylglyoxalyl–Pd moiety (eq 2).[16]

$$\mathrm{PhCOCOCl} + \mathrm{Me_3SiSiMe_3} \xrightarrow{[\mathrm{Pd}]} \mathrm{PhCOSiMe_3} + \mathrm{CO} + \mathrm{ClSiMe_3} \quad (2)$$

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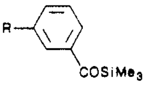
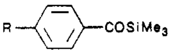
Table II. Preparation of Substituted Benzoyltrimethylsilanes

$$RC_6H_4COCl + Me_3SiSiMe_3 \xrightarrow[\text{neat, 110 °C, 3-20 h}]{{}^1/_2[(\eta^3\text{-}C_3H_5)PdCl]_2 2P(OEt)_3\ (5\ \text{mol}\ \%)} RC_6H_4COSiMe_3$$

entry	R	time, h	yield,[a] %	IR (C=O), cm^{-1}	^{1}H NMR (CDCl$_3$, Me$_4$Si), δ	anal.
Ortho Substituent						
1	Me	3	24	1615	0.30 (s), 2.39 (s), 6.98–7.63 (m)	*f*
2	OMe	4.5	32	1610	0.23 (s), 3.87 (s), 6.81–7.60 (m)	A
3	Cl	4	24 (11)[b]	1620	0.29 (s), 7.00–7.53 (m)	*f*
4	Br	4	11 (11)[b]	1630	0.21 (s), 6.90–7.70 (m)	B
5	CO$_2$Me	4	... (36)[b]			...
6	NO$_2$	20	... (30)[b]			...
Meta Substituent						
7	Me	6	48	1610	0.30 (s), 2.40 (s), 7.23–7.77 (m)	*f*
8	OMe	3	47	1615	0.39 (s), 3.84 (s), 6.90–7.51 (m)	C
9	Cl	18.5	57	1615	0.38 (s), 7.35–7.82 (m)	*f*
10	Br	19	48	1615	0.38 (s), 7.13–7.93 (m)	D
11	CF$_3$	6	52	1625	0.39 (s), 7.38–8.10 (m)	E
12	CO$_2$Me	3	56	1730, 1620	0.40 (s), 3.92 (s), 7.30–8.55 (m)	F
13	CO$_2$Et	5	40	1725, 1620	0.38 (s), 1.39 (t, J = 7.2 Hz), 4.39 (q, J = 7.2 Hz), 7.39–8.62 (m)	G
14	NO$_2$	7	43	1625	0.42 (s), 7.20–8.73 (m)	H
Para Substituent						
15	H	6	78	1610	0.35 (s), 7.25–7.83 (m)	*f*
16	Me	5	81	1615	0.36 (s), 2.37 (s), 7.21 and 7.69 (d, J = 8.4 Hz)[c]	*f*
17	*t*-Bu	7	58	1615	0.37 (s), 1.35 (s), 7.52 and 7.79 (d, J = 8.4 Hz)[c]	*f*
18	OMe	3	48	1615	0.33 (s), 3.82 (s), 6.94 and 7.84 (d, J = 8.4 Hz)[c]	I
19	Cl	18	71	1615	0.35 (s), 7.30 and 7.62 (d, J = 8.4 Hz)	*g*
20	Br	5	48	1615	0.37 (s), 7.59 (br s)[c]	J
21	CF$_3$	12	50	1610	0.38 (s), 7.76 and 7.88 (d, J = 2.4 Hz)[c]	K
22	CO$_2$Me[d]	3	47 (5)[b]	1615	0.38 (s), 3.89 (s), 7.79 and 8.07 (d, J = 8.4 Hz)[c]	L
23	CO$_2$Et	7	39	1620	0.36 (s), 1.37 (t, J = 7.2 Hz), 4.38 (q, J = 7.2 Hz), 7.87 and 8.13 (d, 8.4 Hz)[c]	M
24	CN	18.5	14 (22)[b]	1615	0.39 (s), 7.81 and 7.86 (d, J = 8.5 Hz)[c]	N
25	NO$_2$[e]	2.5	37 (28)[b]	1620	0.40 (s), 7.89 and 8.26 (d, J = 8.4 Hz)[c]	O

[a] Purified by column chromatography followed by short-path distillation. [b] Isolated yield of the corresponding aryltrimethylsilane (decarbonylation product). [c] Para-disubstituted phenyls; an AA'BB' pattern. [d] Mp 53–54 °C (hexane). [e] Mp 97 °C (hexane–ethyl acetate). [f] Known compounds (see ref 4b). [g] Elemental analysis not given (cf. isomers).

Table III. ^{13}C{^{1}H} NMR Data of Meta- and Para-Substituted Benzoyltrimethylsilanes

	chemical shifts, δ								
R	C=O	C-1	C-2	C-3	C-4	C-5	C-6	SiMe$_3$	others
									
H	235.6	141.4 (+12.9)[b]	128.6[a] (+0.13)[b]	127.5[a] (−1.05)[b]	132.6 (+4.13)[b]			−1.31	
Me	235.9	141.5	128.5	138.6	133.4	127.4	125.2	−1.32	Me, 21.4
OMe	235.1	142.6	110.4	160.0	119.4	129.6	121.2	−1.32	OMe, 55.3
Cl	234.3	142.6	127.0	135.1	132.5	130.0	125.9	−1.46	
Br	234.3	142.7	130.2	123.2	135.4	130.0	126.4	−1.46	
CO$_2$Me	235.0	141.4	129.2	135.2	133.4	128.9	131.0	−1.46	CO, 166.4 OMe, 52.4
NO$_2$	233.6	141.9	122.4	148.6	126.8	130.0	132.6	−1.61	
									
Me	234.6	139.1	127.6	129.3	143.3			−1.32	Me, 21.6
OMe	232.7	135.1	129.8	113.7	163.1			−1.24	OMe, 55.4
Cl	234.0	139.4	128.7	128.9	138.9			−1.47	
CO$_2$Me	235.9	144.0	127.1	130.0	133.3			−1.54	CO, 166.3 OMe, 52.4
NO$_2$	235.1	144.9	128.1	124.1	149.9			−1.63	

[a] Interchange of C-2 with C-3 gave inferior shift differences for the calculated chemical shifts of substituted benzoyltrimethylsilanes. [b] Shift differences Δδ for ring carbons taken at 128.5 ppm as a standard of benzene.[14] Calculated chemical shifts are within ±1.5 ppm except for the *p*-nitro group.

Similar decarbonylation of MeCOCOCl has been suggested in a ketone synthesis from oxalyl chloride with the methyltin compound.[17]

The present reaction can be extended to aliphatic acid chlorides and other aroyl chlorides[18] under the standard conditions, giving the corresponding acyltrimethylsilanes

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Table IV. Preparation of Aroyl- and Acyltrimethylsilanes

acid chloride[a]	reactn time, h	products (yield, %)
p-$ClCOC_6H_4COCl$	17	*p*-$Me_3SiCOC_6H_4COSiMe_3$ (6), *p*-$Me_3SiC_6H_4COSiMe_3$ (17)
m-$ClCOC_6H_4COCl$	14	*m*-$Me_3SiCOC_6H_4COSiMe_3$ (32), *m*-$Me_3SiC_6H_4COSiMe_3$ (7), *m*-$HCOC_6H_4COSiMe_3$ (5)[b]
β-$C_{10}H_7COCl$	5.5	β-$C_{10}H_7COSiMe_3$ (32)
2-$(C_4H_3O)COCl$[c]	6	2-$(C_4H_3O)COSiMe_3$ (22)[d]
$C_7H_{15}COCl$	24	$C_7H_{15}COSiMe_3$ (27)[e]
$C_6H_5CH_2COCl$	7	$C_6H_5CH_2COSiMe_3$ (28), $C_6H_5CH_2SiMe_3$ (8)[f]

[a] Under the standard conditions (entry 6, Table I). [b] Presumably formed by hydrolysis of the major product. [c] 2-Furoyl chloride. [d] See ref 18. [e] The corresponding trimethylgermane was obtained in 15% yield (90 °C, 38 h). [f] Decarbonylation product.

in rather inferior yields. Aliphatic acid chlorides presumably suffer from a side reaction, e.g., β-elimination of an intermediate acyl–Pd complex. All results for these derivatives are given in Table IV.

(c) Silicon–Germanium Bimetallic Compounds. There have been relatively few acylgermanes and -stannanes that are generally prepared by the same procedures as those of silicon congeners.[2,3]

It was found that hexamethyldigermane underwent benzoylation faster than hexamethyldisilane under the standard conditions (entry 6, Table I) even at lower reaction temperature (eq 3). Benzoyltrimethylgermane was

$$PhCOCl + Me_3GeGeMe_3 \xrightarrow[70\text{–}110\ °C]{[Pd]} PhCOGeMe_3 + ClGeMe_3 \quad (3)$$

equally obtained at lower temperatures with longer reaction periods: 110 °C (4 h), 90 °C (6.5 h), and 70 °C (69 h), in 78, 69, and 62% yields, respectively. Therefore, it appeared worthwhile to examine the palladium-catalyzed benzoylation of a series of silicon–germanium bimetallic compounds.

In addition to pentamethylphenyldisilane and -digermane, (trimethylsilyl)- and (dimethylphenylsilyl)trimethylgermane were prepared. Intramolecularly competitive benzoylation of these bimetallic compounds was thus carried out under otherwise the same conditions as those of the catalysis of 1 with triethyl phosphite at 110 °C. On the basis of product ratios given in eq 4–7, one may argue the relative reactivity of the groups that undergo benzoylation from these bimetallic compounds.

$$PhCOCl + Me_3SiGeMe_3 \xrightarrow[110\ °C,\ 4.5\ h]{[Pd]} \underset{37\%}{PhCOGeMe_3} + \underset{7\%}{PhCOSiMe_3} \quad (4)$$

$$PhCOCl + Me_3SiSiMe_2Ph \xrightarrow[110\ °C,\ 5.5\ h]{[Pd]} \underset{55\%}{PhCOSiMe_2Ph} + \underset{21\%}{PhCOSiMe_3} \quad (5)$$

$$PhCOCl + PhMe_2SiGeMe_3 \xrightarrow[110\ °C,\ 4\ h]{[Pd]} \underset{21\%}{PhCOGeMe_3} + \underset{10\%}{PhCOSiMe_2Ph} \quad (6)$$

$$PhCOCl + Me_3GeGeMe_2Ph \xrightarrow[110\ °C,\ 5.5\ h]{[Pd]} \underset{55\%}{PhCOGeMe_2Ph} + \underset{7\%}{PhCOGeMe_3} \quad (7)$$

$$\underset{42}{PhMe_2Ge} > \underset{5.4}{Me_3Ge} > \underset{2.6}{PhMe_2Si} > \underset{1.0}{Me_3Si}$$

Scheme I

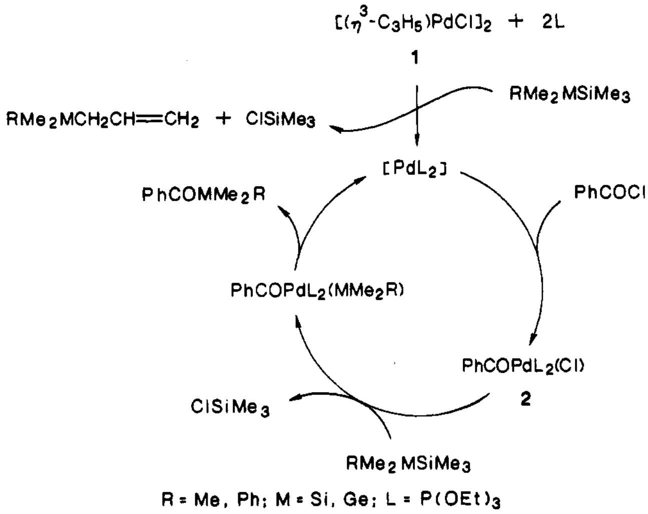

Table V. ^{13}C NMR Substituent Effect on Chemical Shifts[a]

substituent	C-1	ortho	meta	para
Me_3SiCO	+12.7	0.0	−1.2	+4.8
MeCO	+9.1	+0.1	0.0	+4.2
Me_3CCO[b,c]	+9.3	−1.2	−1.2	+1.6

[a] Δδ, ppm (benzene, δ 128.5). [b] Neat sample: Stothers, J. B. *Can. J. Chem.* **1965**, *43*, 498. [c] δ 206.9 (carbonyl carbon).

Thus, the reactivity order given above may well reflect an anionic stability of an RMe_2M (R = Ph, Me; M = Ge, Si) group which is preferentially transmetalated with the electrophilic Pd(II) species and in turn undergoes benzoylation. RMe_2M^- reagents could be envisaged to demonstrate a variety of reactivities toward electrophiles in addition to formal S_N2 behavior.[19]

Attempted catalyzed reaction of benzoyl chloride with *sym*-dichlorotetramethyldisilane, heptamethyltrisilane, and hexamethylditin[20] gave no benzoylation products at all under the conditions employed.

Mechanism of the Reaction. The most plausible catalytic cycle for the reactions may be outlined in Scheme I, which accommodates all mechanistic features given above.

The active catalyst, bis(triethyl phosphite)palladium(0), may be generated from 1. The catalyst precursor 1, in the presence of triethyl phosphite as a supporting ligand, acts as a soft electrophile to cleave the Si–Si bond of hexamethyldisilane (transmetalation)[21] only at elevated temperature, giving the palladium(0) species with concomitant formation of allyltrimethylsilane and chlorotrimethylsilane. Acid chloride adds oxidatively to PdL_2, generating a benzoylchloropalladium(II) complex (2), which undergoes transmetalation with hexamethyldisilane to accommodate a trimethylsilyl group and, in turn, reductively eliminates the product benzoyltrimethylsilane.

The observed order of the ease of group transfer in the bimetallic compounds appears to coincide with the relative reactivity in the transmetalation step.

However, it is still controversial why triethyl phosphite is the most suitable supporting ligand examined in the catalytic reaction. It may be assumed that the trans-

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Table VI. Elemental Analyses[a] of Substituted Benzoyltrimethylsilanes

anal.	R	mol formula	C	H	others
A	*o*-OCH_3	$C_{11}H_{16}O_2Si$	63.49 (63.42)	7.75 (7.74)	
B	*o*-Br	$C_{10}H_{13}BrOSi$	46.87 (46.70)	5.32 (5.09)	
C	*m*-OCH_3	$C_{11}H_{16}O_2Si$	63.48 (63.42)	7.81 (7.74)	
D	*m*-Br	$C_{10}H_{13}BrOSi$	46.82 (46.70)	5.23 (5.09)	
E	*m*-CF_3	$C_{11}H_{13}F_3OSi$	53.73 (53.64)	5.30 (5.32)	
F	*m*-CO_2CH_3	$C_{12}H_{16}O_3Si$	60.93 (60.98)	6.66 (6.82)	
G	*m*-$CO_2C_2H_5$	$C_{13}H_{18}O_3Si$	62.20 (62.37)	7.32 (7.25)	
H	*m*-NO_2	$C_{10}H_{13}NO_3Si$	54.09 (53.79)	5.83 (5.87)	N, 6.06 (6.27)
I	*p*-OCH_3	$C_{11}H_{16}O_2Si$	62.92 (63.42)	7.66 (7.74)	
J	*p*-Br	$C_{10}H_{13}BrOSi$	46.25 (46.70)	5.02 (5.09)	Br, 30.35 (31.07)
K	*p*-CF_3	$C_{11}H_{13}F_3OSi$	53.77 (53.64)	5.48 (5.32)	
L	*p*-CO_2CH_3	$C_{12}H_{16}O_3Si$	60.68 (60.98)	6.77 (6.82)	
M	*p*-$CO_2C_2H_5$	$C_{13}H_{18}O_3Si$	62.41 (62.37)	7.12 (7.25)	
N	*p*-CN	$C_{11}H_{13}NOSi$	65.02 (64.98)	6.18 (6.45)	N, 6.84 (6.89)
O	*p*-NO_2	$C_{10}H_{13}NO_3Si$	53.89 (53.79)	5.88 (5.87)	N, 6.37 (6.27)

[a] Calculated values are given in parentheses.

metalation step is facilitated by an electrophilic attack of **2** with L = $P(OEt)_3$ rather than L = PPh_3 on the bimetallic compounds; i.e., the less basic phosphite seems to make **2** a better electrophile.

$Pd(PPh_3)_4$ is shown to be almost ineffective in the reaction, while $(PPh_3)_2PdCl_2$ can act as a catalyst precursor.[13,18] Therefore, excess triphenylphosphine has presumably a deactivation effect on the active catalyst PdL_2. Similar deactivation has already been discussed in the ketone synthesis from acid chlorides and organotin compounds catalyzed by palladium complexes.[17]

Any participation of diethyl benzoylphosphonate, which is readily obtained from benzoyl chloride and triethyl phosphite by the Arbuzov reaction, in the benzoylsilane synthesis was precluded by the following independent reactions. First, it was confirmed that when an equimolar mixture of triethyl phosphite and palladium complex **1** in benzene was heated at reflux temperature with benzoyl chloride (1 equiv), no trace of diethyl benzoylphosphonate was formed. Secondly, attempted reaction of diethyl benzoylphosphonate with hexamethyldisilane in the presence of benzoyl chloride and **1** (5 mol %) at 110 °C did not proceed to form diethyl trimethylsilyl phosphite and benzoyltrimethylsilane, if any, resulting in the decomposition of **1**.[22]

Experimental Section

General Comments. All boiling and melting points are uncorrected. ^1H NMR spectra were obtained on Hitachi R24 spectrometer with Me_4Si as an internal standard in $CDCl_3$. ^{13}C NMR spectra were measured on a JEOL FX-90Q or FX-100 spectrometer. IR spectra (mostly in neat) were recorded on JASCO IRA-2 spectrophotometer.

Materials. Acid chlorides (benzoyl bromide and benzoyl fluoride) were either obtained commercially or prepared by known procedures and distilled prior to use. $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (**1**),[23] $Pd(PPh_3)_4$,[24] and $[P(OMe)_3]_2PdCl_2$[25] were also prepared by the standard methods. All bimetallic compounds used in this study were prepared according to the literature method indicated: $Me_3SiSiMe_3$,[26] $PhMe_2SiSiMe_3$,[26] $Me_3SiSiMe_2SiMe_3$,[26] $ClMe_2SiSiMe_2Cl$,[26] $Me_3GeGeMe_3$,[27] $PhMe_2GeGeMe_3$,[28] $Me_3SiGeMe_3$,[29] $PhMe_2SiGeMe_3$,[30] and $Me_3SiGeMe_2Ph$.[30]

Examination of Palladium Catalyst Systems for the Preparation of Benzoyltrimethylsilane. An equimolar mixture of hexamethyldisilane and benzoyl chloride (2.2-mmol each) in dry toluene (1.5 mL) and pentadecane (1.0 mmol) as an internal standard was heated at 80–110 °C under argon in the presence of four different kinds of palladium complexes with or without added triphenylphosphine or triethyl phosphite.

Conversion of the reaction in a given time and the ratio of $PhCOSiMe_3/PhSiMe_3$ were determined by GLC analysis (silicone DC-550, 3 mm × 3 m, at 140 °C). The results are given in Table I.

When other solvents were used (heptene, THF, 1,2-dichloroethane, and HMPA), all but toluene exhibited either retardation or deterioration of the catalysis.

Preparation of Substituted Benzoyltrimethylsilanes. General Procedure. In a screw-capped glass tube (10 mL) were placed **1** (27.4 mg, 0.15 mmol) and triethyl phosphite (49.8 mg, 0.30 mmol) under argon. Hexamethyldisilane (0.64 mL, 3.3 mmol) was added, and the mixture was stirred magnetically for 5 min at room temperature, during which time the mixture became a yellowish suspension. Freshly distilled substituted benzoyl chloride (3.0 mmol) was then added, and the whole mixture was heated at 110 °C for 3–20 h. When solvent was required, toluene (2.1 mL) was appropriately added to keep the mixture homogeneous.

After the reaction was completed (usually a palladium mirror formed), the reaction mixture was cooled and subjected directly to column chromatographic separation (silica gel, hexane–ether) to afford the corresponding aryltrimethylsilane and/or substituted benzoyltrimethylsilane. The latter compound was further purified by short-path distillation (Kugelrohr; bp 90–130 °C (2 torr)) to give an analytically pure sample usually as a clear yellow oil. Yield, IR, ^1H NMR, and analytical data of 25 substituted benzoyltrimethylsilanes are summarized in Table II. $^{13}C\{^1H\}$ NMR data for meta- and para-substituted derivatives are given in Table III.

On the basis of calculated additive substituent effects, the substituent effect of the Me_3SiCO group on chemical shifts was proposed (Table V).[14b]

Palladium Complex Catalyzed Acylation of Hexamethyldisilane (Table IV). In the same manner as that of the general procedure, acylation of hexamethyldisilane using several acid chlorides was carried out. Physical and analytical data for certain products are given. *p*-$Me_3SiCOC_6H_4COSiMe_3$: ^1H NMR ($CDCl_3$) δ 0.39 (s), 7.89 (s); IR (KBr) 1600 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2Si_2$: C, 60.38; H, 7.96. Found: C, 60.31; H, 7.78. *p*-$Me_3SiC_6H_4COSiMe_3$: ^1H NMR δ 0.28 (s), 0.35 (s), 7.68 and 7.78 (d, AA′BB′, *J* = 8.4 Hz). *m*-$Me_3SiCOC_6H_4COSiMe_3$: ^1H NMR δ 0.40 (s), 7.39–8.37 (m); IR (KBr) 1605 cm^{-1}. Anal. Calcd for

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[22] A catalytic cycle is presumed:

$$PhCOP(O)(OEt)_2 + Me_3SiSiMe_3 \xrightarrow{1} PhCOSiMe_3 + (Me_3SiO)P(OEt)_2$$

$$(Me_3SiO)P(OEt)_2 + PhCOCl \rightarrow PhCOP(O)(OEt)_2 + ClSiMe_3$$

The latter reaction does occur easily (see Experimental Section).

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$C_{14}H_{22}O_2Si_2$: C, 60.38; H, 7.96. Found: C, 60.21; H, 7.77. *m*-$Me_3SiC_6H_4COSiMe_3$: ^1H NMR δ 0.30 (s), 0.49 (s), 7.26–8.13 (m); IR (neat) 1610 cm^{-1}. Anal. Calcd for $C_{13}H_{22}OSi_2$: C, 62.34; H, 8.85. Found: C, 62.12; H, 8.78. *m*-$HCOC_6H_4COSiMe_3$: ^1H NMR δ 0.40 (s), 7.46–8.52 (m), 10.21 (s); IR (neat) 1700, 1620 cm^{-1}. β-$C_{10}H_7COSiMe_3$: ^1H NMR δ 0.44 (s), 7.43–8.42 (m); IR (neat) 1600, 1590 cm^{-1}. (2-C_4H_3O)$COSiMe_3$: bp 130 °C (27 torr); ^1H NMR δ 0.35 (s), 6.48 (dd), 7.03 (d), 7.53 (m); IR (neat) 1610 cm^{-1}. $C_7H_{15}COSiMe_3$: ^1H NMR (CCl_4) δ 0.16 (s), 0.89 (t), 1.26 (br s), 2.48 (t); IR (neat) 1620 cm^{-1}. $C_6H_5CH_2COSiMe_3$: bp 110 °C (3 torr); ^1H NMR (CCl_4) 0.04 (s), 3.69 (s), 7.17 (m); IR (CCl_4) 1640 cm^{-1}.

Palladium Complex Catalyzed Competitive Benzoylation of Bimetallic Compounds. All reactions were carried out under the standard conditions (entry 6, Table I), and respective yields of benzoylated derivatives are indicated in eq 3–7. Some Physical data are given below. $PhCOGeMe_3$:[31] ^1H NMR ($CDCl_3$) δ 0.50 (s), 7.34–7.92 (m); IR (neat) 1625, 1595 cm^{-1}. $C_7H_{15}COGeMe_3$: ^1H NMR δ 0.33 (s), 0.87 (t, J = 4.8 Hz), 1.07–1.91 (m), 2.60 (t, J = 6.9 Hz); IR (neat) 1660 cm^{-1}. $PhCOSiMe_2Ph$:[32] ^1H NMR 0.63 (s), 7.08–7.90 (m). $PhCOGeMe_2Ph$:[33] ^1H NMR δ 0.72 (s), 7.20–7.85 (m).

Controlled Reactions of Benzoyl Chloride with Triethyl Phosphite or Diethyl Trimethylsilyl Phosphite. Authentic Samples. (1) Preparation of Diethyl Trimethylsilyl Phosphite. To a solution of diethyl phosphite (19.4 mL, 0.15 mol) and triethylamine (25.2 mL, 0.18 mol) in dry ether (100 mL) was added dropwise chlorotrimethylsilane (22.8 mL, 0.18 mol) over a period of 45 min. The reaction mixture was stirred at room temperature for 5 h and refluxed for additional 4 h. Voluminous precipitates were filtered, and the filtrate was concentrated. Distillation of the residue gave $(EtO)_2P(OSiMe_3)$ (26.6 g, 84% yield), bp 55–57 °C (12 torr). **(2) Preparation of Diethyl Benzoylphosphonate.** To a solution of diethyl trimethylsilyl phosphite (8.42 g, 40 mmol) in benzene (20 mL) was added benzoyl chloride (4.4 mL, 38 mmol). The mixture was stirred for 2.5 h and then concentrated in vacuo. The residue was distilled, bp 154 °C (6 torr), to give $PhCOP(O)(OEt)_2$ (4.9 g, 54% yield).

Attempted Arbuzov Reaction. An equimolar mixture of triethyl phosphite and palladium complex 1 (0.2 mmol) in dry benzene (0.5 mL) was heated at 100 °C for 7 h with benzoyl chloride (0.2 mmol) under argon. No diethyl benzoylphosphonate was detected by GLC analysis.

Attempted Palladium Complex Catalyzed Reaction of Diethyl Benzoylphosphonate with Hexamethyldisilane. An equimolar (3-mmol each) mixture of hexamethyldisilane, benzoyl chloride, and diethyl benzoylphosphonate prepared above in dry toluene (2 mL) was heated at 110 °C under an argon atmosphere in the presence of 1 (0.15 mmol, 5 mol %). Gradual decomposition of 1 took place, and no appreciable reaction to form benzoyltrimethylsilane was observed by GLC analysis.

Acknowledgment. Support of the Grant-in-Aid from the Ministry of Education, Japan (No. 555341), is gratefully acknowledged. We thank Toshiba Silicone Co. Ltd. for a gift of chlorosilanes.

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Substituent Effects of Substituted Benzoyltrimethylsilanes on Their Ultraviolet Spectral Properties

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Received September 2, 1986

A series of meta- and para-substituted benzoyltrimethylsilanes have been prepared, and their ultraviolet spectra are recorded. Correlation of the wavenumber of the n → π^* absorption maxima with the dual substituent parameters (DSP) has been examined, giving the susceptibility parameters $\lambda = \rho_R/\rho_I = 2.54$. Implication of this treatment has briefly been discussed.

One of the outstanding features of α-silyl ketones is their yellow color, which stems from the long wavelength (~420 nm) absorption.[1] These transitions have been assigned as n → π^*.[2] Bock et al.[2d] have discussed the remarkable long-wavelength shifts of the n → π^* transition of benzoylsilanes mainly in terms of strong electron-releasing effects of R_3Si groups on the oxygen lone pair n_O. Also, the importance of metal–carbon bond mixing with adjacent

Table I. Solvent Effect on the Absorption Maxima of Benzoyltrimethylsilane

		absorptn maxima			
solv	concn × 10^5,[a] mol/L	$\pi \rightarrow \pi^*$, nm	$10^{-4}\epsilon$	n → π^*,[b] nm	ϵ
hexane	5.65	250.0	1.13	423.0	119
cyclohexane	5.83	250.5	1.18	423.0	130
THF	8.47			420.0	116
ethanol	5.77	252.5	0.95	415	101
$PhCOCMe_3$ in hexane		238	0.88	320	103

[a] For $n \rightarrow \pi^*$ measurements; diluted as 1/100 for $\pi \rightarrow \pi^*$. [b] The most intense peak in a fine structure.

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0276-7333/87/2306-0979$01.50/0