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A new and efficient method for the synthesis of bromosilanes from hydrosilanes using $Br_3CCOOEt/PdCl_2$ as the catalyst

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ABSTRACT

Bromosilanes were prepared conveniently and efficiently via the reaction of hydrosilanes and $Br_3CCOOEt$ in the presence of a catalytic amount of $PdCl_2$ in refluxing THF over 15 min in high yields. The developed methodology was further applied for the one-pot synthesis of silyl ethers and silyl esters in excellent yields.

Halosilanes can be used for ester and ether cleavage, carbonyl addition processes, and halosilane-accelerated carbon–carbon bond-forming reactions.[1] Specifically for bromosilanes, depending on the reaction conditions, they can be used for both the protection[2] and deprotection[3] of functional groups. Cleavage of cyclic orthoesters is also possible.[4]

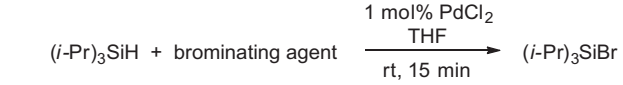
Several methods have been reported for the preparation of bromosilanes, such as reactions of triphenylsilanol with $SiBr_4$,[5] trialkylarylsilanes with Br_2,[6] silane with AgBr,[7], and selenosilanes and Br_2.[8] Reaction of $tBu_2SiH–NH–SiPh_3$ and *N*-bromosuccinimide also afforded bromosilane which was isolated as a by-product.[9]

Bromosilanes can also be prepared directly from hydrosilanes and bromine,[2,10] but bromine is highly toxic. Novel methods for bromosilane preparation from hydrosilanes have been reported using $PdCl_2$ or $NiCl_2$,[11] or Cu(II)-based reagents,[12] however, these methods still require long reaction times or stoichiometric amounts of copper.

Our group has studied extensively the reactions of halogenating agents[13] and we have previously reported the transformation of hydrosilanes into chlorosilanes.[13i] Bromosilanes are much more reactive than chlorosilanes because of the weaker Si–Br bond.[1,14] However, publications on bromosilanes are not as prominent as those on chlorosilanes because of their synthetic challenge and low stability. Hence, we have developed an efficient method for the preparation of bromosilanes using $Br_3CCOOEt$[13g] in the presence of a catalytic amount of $PdCl_2$, and subsequently used them for the in situ preparation of silyl esters and ethers. The mechanism of the reaction is likely to be similar to that of the chloro counterpart.[13i]

Various brominating agents were initially screened for the bromination of triisopropylhydrosilane (TIPS-H) to furnish the corresponding triisopropylbromosilane (TIPS-Br) (Table 1). The yields of TIPS-Br were quantified by ^1H NMR spectroscopy using toluene as an internal standard.

Table 1
The effect of brominating agents on the conversion of TIPS-H into TIPS-Br



Entry	Brominating agent	Equivalents (mmol)	Yield[a] (%) TIPS-Br	Recovery[a] (%) TIPS-H	MB[c] (%)
1	None	–	0	100	100
2	CBr_4	0.75	39	53	92
3	Br_3CCOOH	1.00	36	64	100
4	$Br_3CCOOEt$	1.00	44	55	99
5[b]	$Br_3CCOOEt$	1.00	0	100	100
6	$Br_3CCOOEt$	1.25	60	39	99
7	$Br_3CCOOEt$	1.50	67	29	96
8	$CHBr_3$	1.00	9	91	100
9	$Br_2CHCOOH$	1.50	7	91	98
10	$Br_2CHCOOEt$	1.50	6	92	98
11	$CH_2{=}CHCH_2Br$	3.00	5	93	98
12	CH_3CH_2Br	3.00	9	90	99

[a] Determined by ^1H NMR spectroscopy using toluene as an internal standard.
[b] The reaction was carried out in the absence of the Pd(II) catalyst.
[c] Mass balance.

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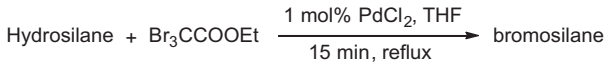
Table 1 reveals that using CBr_4, Br_3CCOOH and $Br_3CCOOEt$ produced TIPS-Br in moderate yields (entries 2–4) while other brominating agents yielded minimal amounts of TIPS-Br (entries 8–12). Due to the toxicity of CBr_4 and the low solubility of Br_3CCOOH in the reaction medium, $Br_3CCOOEt$ was the best choice for further study. Addition of a Pd(II) catalyst was also found to be essential for this reaction (entry 5). Increasing the amount of $Br_3CCOOEt$ from 1 to 1.5 equiv improved the yield to 67% at ambient temperature.

The reaction conditions were further investigated by varying the solvent, catalyst, reaction temperature, and amount of $Br_3CCOOEt$, and the optimized conditions are as follows: TIPS-H/$PdCl_2$/$Br_3CCOOEt$ = 1:0.01:1.25 at reflux in THF for 15 min which produced TIPS-Br in quantitative yield. The results indicated that THF and CH_3CN were suitable solvents for this reaction giving the product in high yield. When the reaction temperature was raised to reflux (THF), the number of equivalents of $Br_3CCOOEt$ could be reduced from 1.50 to 1.25.

This method was successfully applied to various hydrosilanes (Table 2). Surprisingly, increasing the amount of $Br_3CCOOEt$ only improved the yield of Ph_3SiH, but the amounts of products were almost the same for other substrates.

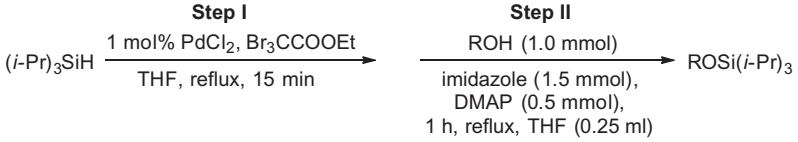
Table 2
The conversion of hydrosilanes into bromosilanes using a Pd(II) catalyst and $Br_3CCOOEt$

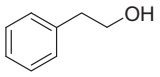
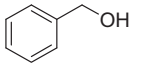
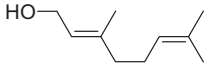


Entry	Hydrosilane	Equivalents (mmol)	Yield[a] (%) Si–Br	% Recovery[a] (%) Si–H	MB (%)
1	$(i\text{-Pr})_3SiH$	1.25	100	0	100
2	Ph_3SiH	1.25	65	35	100
3	Ph_3SiH	1.50	75	24	99
4	Ph_3SiH	1.75	90	9	99
5	Ph_2ClSiH	1.25	82	18	100
6	$PhMe_2SiH$	1.25	51	47	98
7	Et_3SiH	1.25	60	37	97
8	$t\text{-BuMe}_2SiH$	1.25	61	35	96

[a] Determined by ^1H NMR spectroscopy.

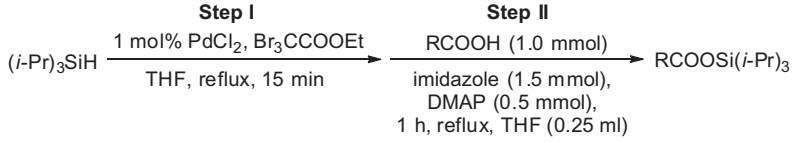
Table 3
The one-pot synthesis of silyl ethers

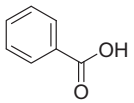
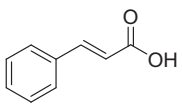
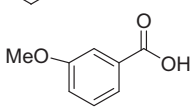


Entry	Alcohol	Yield (%)
1		86[a]
2		100[b]
3		100[b]

[a] Separated on an alumina column.
[b] Determined by ^1H NMR spectroscopy.

Table 4
The one-pot synthesis of silyl esters



Entry	Carboxylic acid	Yield[a] (%)
1		100
2		100
3		100

[a] Determined by ^1H NMR spectroscopy.

In addition, this protocol could be further applied for the one-pot synthesis of silyl ethers and esters by reacting the in situ generated bromosilane with the appropriate alcohol or carboxylic acid (Tables 3 and 4). The target silyl ethers and esters were obtained in high yields and the reaction times were shorter than when using chlorosilane.[15]

In conclusion, $Br_3CCOOEt$ coupled with a catalytic amount of $PdCl_2$ has been utilized as an efficient brominating system for the bromination of hydrosilane. The method developed could be successfully applied to other hydrosilanes and further employed in a one-pot procedure for the synthesis of silyl ethers and esters in high yields.

A typical procedure for the preparation of bromosilanes from hydrosilanes: To a stirred solution of $PdCl_2$ (1 mol %, 1.8 mg) and $Br_3CCOOEt$ (1.25 equiv, 1.25 mmol, 185 μL) in THF (0.25 mL) was added TIPS-H (1 equiv, 1.0 mmol, 205 μL) and the mixture was heated at reflux in THF under an N_2 atmosphere for 15 min. The crude mixture was analyzed by ^1H NMR spectroscopy with the addition of toluene (1 equiv, 1.0 mmol, 106 μL) as an internal standard. In a typical case, TIPS-Br (229 mg, 96% yield) was isolated by filtration and vacuum distillation.

For the one-pot synthesis of silyl ethers and esters, after stirring the mixture described above for 15 min, the alcohol or acid (1 mmol), DMAP (0.5 mmol), and imidazole (1.5 mmol) were added and the mixture was stirred at reflux for 1 h. After cooling, the yield of product was either determined by ^1H NMR spectroscopy using toluene (1 equiv, 1.0 mmol, 106 μL) as an internal standard or was isolated by column chromatography on alumina.

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