Phosphazene base-promoted functionalization of aryltrimethylsilanes†

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The activation of Ar–Si bonds in aryltrimethylsilane was investigated using a catalytic amount of *t*-Bu-P4 base and selective functionalizations of aryltrimethylsilanes in the absence of strong electron withdrawing groups on the aromatic rings were accomplished.

Aryltrimethylsilanes have been used as important synthons and various desilylative functionalizations have been investigated to date.[1] Among these, anion mediated generation of aryl anions is one of the most important methods for selective bond formation.[2] However, anion promoted activation has been limited to aryltrimethylsilanes with strong electron withdrawing groups on the aromatic rings, due to the instability of the generated aryl anions. Phosphazene bases[3] developed by Schwesinger and proazaphosphatranes[4] developed by Verkade are known to be strong non-metallic organic superbases (Fig. 1). Among them, *t*-Bu-P4 base shows extremely high basicity and has been used in various selective deprotonative transformations.[5] While the strong affinity of *t*-Bu-P4 base for protons is regarded as synthetically useful, the ability of *t*-Bu-P4 base to activate organometallic compounds is largely undocumented.[6] In a recent paper, we reported that *t*-Bu-P4 base could be used as an excellent catalyst to activate organosilicon compounds and demonstrated the possibility of catalytic activation of phenyltrimethylsilane.[7] In order to disclose the scope and limitation of this novel selective conversions of phenyltrimethylsilanes catalyzed by *t*-Bu-P4 base, we have now surveyed the functionalizations of various aryltrimethylsilanes in the presence of catalytic phosphazene base.

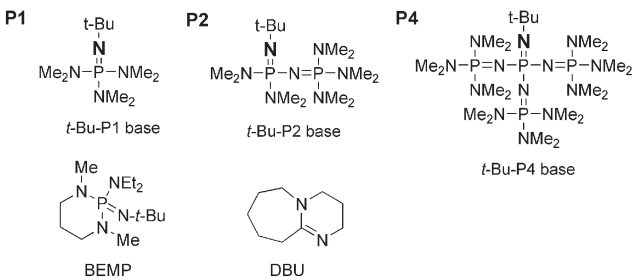

Fig. 1 Phosphazene bases and DBU.

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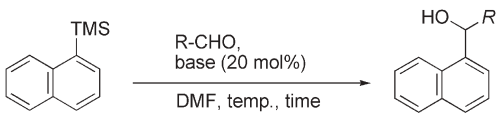
1-Trimethylsilylnaphthalene (**1**) was chosen as a substrate for the optimization of suitable conditions and the reactions of **1** with aldehydes in the presence of various strong organic bases were examined. The reaction of **1** with pivaldehyde in the presence of 20 mol% *t*-Bu-P4 base proceeded smoothly at room temperature to give the alcohol **2a** in 91% yield (Table 1, entry 1). Other phosphazene bases with weaker basicities, such as *t*-Bu-P2 base and BEMP showed no catalytic activity (Table 1, entries 2, 3). As one of the conventional strong organic bases, DBU was employed in conjunction with pivaldehyde and was found to be inactive. CsF was then examined as a fluoride anion donor, but no carbon–silicon bond cleavage was observed. The reactions with other aldehydes were examined, that with benzaldehyde was found to proceed somewhat slowly at room temperature. However, if the reaction temperature was elevated to 80 °C then the product **2b** was obtained in 61% yield. Other aryl aldehydes with electro-donating groups were also employed as electrophiles and the reactions proceeded smoothly at room temperature. Interestingly electron-rich arylaldehydes seemed to react faster than benzaldehyde (Table 1, entries 7–8).

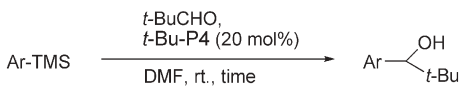
Table 1



Entry	Base	R	Temp./°C	Time/h	Product	Yield (%)
1	*t*-Bu-P4	*t*-Bu	rt	1	**2a**	91
2	*t*-Bu-P2	*t*-Bu	rt	24	**2a**	0
3	BEMP	*t*-Bu	rt	24	**2a**	0
4	DBU	*t*-Bu	rt	24	**2a**	0
5	CsF	*t*-Bu	rt	24	**2a**	0
6	*t*-Bu-P4	Ph	80	6	**2b**	61
7	*t*-Bu-P4	4-$MeOC_6H_4$	rt	1	**2c**	78
8	*t*-Bu-P4	2-$MeOC_6H_4$	rt	1	**2d**	68

The reactions of other aryltrimethylsilanes were subsequently examined. 2-Trimethylsilylnaphthalene reacted with pivalaldehyde in the presence of *t*-Bu-P4 base at room temperature to give the alcohol **4a** in 68% yield (Table 2, entry 1). 4-Fluorophenyltrimethylsilane **3b** and 4-bromophenyltrimethylsilane **3c** gave the corresponding alcohols **4b** and **4c** in 64% and 73% yields, respectively (Table 2, entries 2, 3). Similarly, 4-trifluoromethylphenyltrimethylsilane (**3d**) and 2-trifluoromethylphenyltrimethylsilane (**3e**) reacted smoothly to give the alcohols **4d** and **4e** in 69% and 73% yields, respectively (Table 2, entries 4, 5). 4-Methoxycarbonylphenyltrimethylsilane **3f** reacted to give the alcohol **4f** in 46% yield (Table 2, entry 6). The reactions of

Table 2

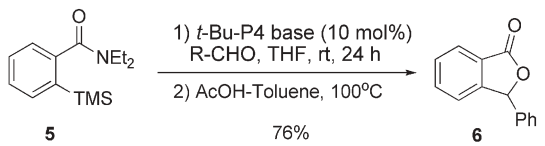


3a-i 4a-i

Entry	Ar	Time/h	Product	Yield (%)
1	2-Naphthyl (**3a**)	3	**4a**	68
2	4-FC_6H_4 (**3b**)	1	**4b**	64
3	4-BrC_6H_4(**3c**)	1	**4c**	73
4	4-$CF_3C_6H_4$(**3d**)	2	**4d**	69
5	2-$CF_3C_6H_4$(**3e**)	1	**4e**	73
6	4-$MeOOCC_6H_4$(**3f**)	1	**4f**	46
7	2-Pyridyl(**3g**)	1	**4g**	67
8	3-Pyridyl(**3h**)	1	**4h**	80
9	2-Thienyl(**3i**)	1	**4i**	81

heteroaryltrimethylsilanes were then examined. 2-Pyridyltrimethylsilane **3g** and 3-pyridyltrimethylsilane **3h** reacted smoothly to give the alcohols **4g** and **4h** in 67% and 80% (Table 2, entries 7, 8). 2-Thienyltrimethylsilane **3i** also reacted to give the alcohol **4i** in 81% yield (Table 2, entry 9).

2-Trimethylsilylated benzamide was now reacted with benzaldehyde to give the 1,2-adduct which was treated with AcOH–toluene to give the phthalide **6** in 76% yield (Scheme 1). Phthalides have been used as precursors for the synthesis of anthraquinones, though in the previous report of this, excess CsF was used for the same carbodesilylation of **5** and the yield of **6** was reported to be 48%.[8]



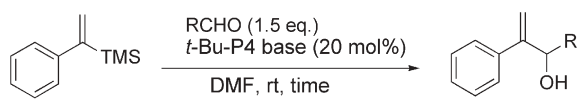
5 76% 6

Scheme 1

Additionally, the vinylsilane **7** was reacted with pivaldehyde in the presence of *t*-Bu-P4 base and the allyl alcohol **8a** was obtained in 56% yield (Table 3, entry 1). Arylaldehydes were also used as electrophiles to give the allyl alcohols **8b**, **8c** (Table 3, entries 2, 3).

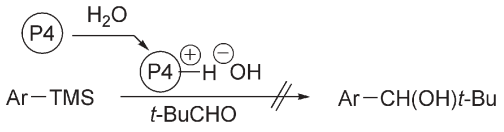
As for the mechanism of the carbon–silicon bond activation, the participation of phosphazenium hydroxide formed by the presence of a trace amount of water cannot be avoided and we examined the reactivity of phosphazenium hydroxide toward the activation. When adding the same equivalent of water to *t*-Bu-P4 base, the catalytic activity was found to be completely lost (Scheme 2).

Table 3

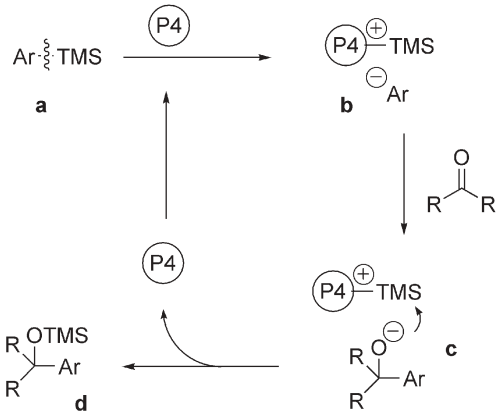


7 8a-c

Entry	R	Time/h	Product	Yield (%)
1	*t*-Bu	2	**8a**	56
2	2-$MeOC_6H_4$	1	**8b**	58
3	4-$MeOC_6H_4$	2	**8c**	52



Scheme 2



Scheme 3

The mechanism of the catalytic reaction is speculated as shown in Scheme 3. The directed interaction of *t*-Bu-P4 base and the trimethylsilyl group activates the carbon–silicon bond to form a highly reactive phosphazenium species (**b**) which reacts with carbonyl compounds to give a 1,2-adduct (**c**) that undergoes silylation of the oxy anion to release *t*-Bu-P4 base.

In summary, it is found that arylsilanes can be carbodesilylated by the use of *t*-Bu-P4 base as a promoter and the selective functionalizations of arylsilanes possessing no strong electron-withdrawing group can be acomplished. *t*-Bu-P4 base is already commercially available as a dry hexane solution and can be used as a catalyst without drying. Further investigations on the scope and limitation of the *t*-Bu-P4 base-promoted reaction of arylsilanes and the mechanistic studies on this carbon–silicon activation are underway.

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