Note

Triallyl(aryl)silanes serve as a convenient agent for silicon-based cross-coupling reaction of aryl halides

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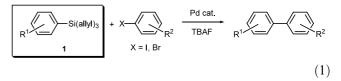Dedicated to Professor J.P. Genêt on the occasion of his 60th birthday

Abstract

Triallyl(aryl)silanes, stable and easily accessible arylsilanes, were found to react with aryl bromides in the presence of a palladium catalyst ($PdCl_2$–PCy_3) and tetrabutylammonium fluoride (TBAF) in good yields. The scope of the reaction is broad, and a wide variety of functional groups are tolerant. Allyl groups on Si are readily cleaved upon treatment with TBAF to form fluorosilanes, silanepolyols, siloxanes and/or their mixed forms, which might be responsible for high efficiency of the reaction.
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Transition metal-catalyzed cross-coupling reaction of arylmetals with aryl halides or pseudo halides is now a straightforward way to construct biaryls that play important roles in many functional organic molecules such as electronic materials and pharmaceuticals [1]. Of organometallic reagents employed for this reaction, organosilicon compounds are attractive in view of availability, stability and non-toxicity [2]. We and others have demonstrated that aryl(halo)silanes [3], trialkoxy(aryl)silanes [4], arylsilanols [5] and poly(phenylsiloxane) [6] can be employed for this reaction. However, these arylsilanes require at least one heteroatom on silicon to enhance the electrophilicity and thus are generally sensitive to water, a base and an acid. Stable all-carbon-substituted arylsilanes would overcome these drawbacks. As for alkenylsilanes, we recently reported that alkenyl(2-thienyl)silanes react with aryl- and alkenylhalides under very mild conditions [7]. This reaction has recently been applied to the stereocontrolled synthesis of poly(*p*-phenylenevinylene)s by Ozawa and Katayama [8]. They also reported that alkenyl[3,5-bis(trifluoromethyl)phenyl]silanes and alkenyl(4-tri-

fluoromethylphenyl)silanes are also effective [9]. Denmark demonstrated that alkneylsilacyclobutanes are excellent coupling partners [10]. Yoshida and Itami also reported that alkenyl(2-pyridyl)dimethylsilanes are effective [11]. Very recently, Trost reported alkenyl(benzyl)dimethylsilanes [12]. In these reactions, (hetero)aryl or benzyl group acts as a good leaving group and silacyclobutane undergoes ring-opening reaction upon treatment with fluoride ion to form possibly alkenylsilanols and/or alkenylsiloxanes [13]. We also found that allyl group on silicon atom worked in a manner similar to 2-thienyl group [14]. However, these strategies have been limited only to cross-coupling of alkenylsilanes. Herein we report that triallyl(aryl)silanes (**1**) are stable toward moisture, bases and acids [15], and react with aryl bromides and an aryl iodide smoothly in good yields in the presence of a palladium catalyst and TBAF (Eq. (1)).

$$(1)$$

First, we examined the reaction of triallyl(phenyl)silane (**1a**) [16] with 4-iodobenzotrifluoride (**2**) under

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various conditions. After treatment of **1a** (1.1 mmol) with TBAF (4.4 mmol) in DMSO–H$_2$O (10:1) at room temperature, the mixture was treated with **2** and Pd catalyst (5 mol%) (Scheme 1). Among various catalyst systems examined, the one consisting of PdCl$_2$ and PCy$_3$ (1:2) was found to be optimal, and the corresponding biaryl was obtained in 97% yield (Table 1, entry 1) [17]. Other ligands (PPh$_3$, P(t-Bu)$_3$ and 1,3-bis(diphenylphosphino)propane), silanes (diallyl(methyl)phenylsilane and allyl(dimethyl)phenylsilane), and solvents (DMF–H$_2$O, dioxane–H$_2$O, toluene–H$_2$O, and DMSO) were inferior [18].

The scope of the present reaction is demonstrated in Table 1. Since the reaction of 4-bromobenzotrifluoride (entry 1) proceeded similarly (95%), the study was conducted using aryl bromides having either an electron-withdrawing or -donating group at 4- and/or 3-position to give coupled product in good yields (entries 2–11). In some cases (entries 6, 8, 9 and 11), a different DMSO–H$_2$O ratio led to a slight increase of yields, though the effect of the amount of water is unclear at present. Sterically demanding substrates also gave the corresponding biaryls in high yields (entries 12–15). Heteroaryl bromides were also applicable to the present reaction. Thus, 2-bromopyridine and 3-bromobenzothiophene afforded the products in good yields (entries 16 and 17).

Next, variously substituted triallyl(aryl)silanes [19] were examined as shown in Table 2. Although electron-rich 4-methoxyphenyl coupled with electron-rich and poor aryl bromides in high yields (entries 1–3), 4-trifluoromethylphenyl- and 2-methylphenylsilane reacted in modest yields due presumably to their lower nucleophilicity and steric hindrance (entries 4 and 5), respectively. In these cases, volatile protonolysis products of coupling partners might be formed since GC showed no starting materials and only a small amount of homo-coupling of aryl bromide other than the desired biaryls.

Although we could not identify the reactive intermediate directly from **1a**, treatment of allyldimethyl(phenyl)silane, instead of **1a**, with TBAF in DMSO–H$_2$O led to the formation of silanol (**3**) and siloxane (**4**) by GC–MS (Scheme 2). Thus, three allyl groups on Si would leave upon treatment with TBAF and water to form possibly fluorosilanes, silanepolyols, siloxanes and/or their mixed forms. Some evidence is presented by Denmark [13], Yoshida [11] and us [5]. Three oxygen atoms make Si atom acidic enough to accept fluoride ion to form reactive pentacoordinate silicates. Since diallyl(methyl)arylsilane or allyl(dimethyl)arylsilanes were not effective for the present reaction as mentioned above, arylsilanediols or arylsilanols would not be active under the present condition presumably due to less acidity of Si, although we and
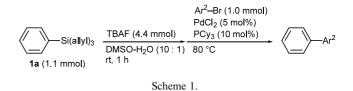
Scheme 1.

Table 1
Cross-coupling reaction of triallyl(phenyl)silane with aryl bromides [a]

entry	Ar^2–Br	time (h)	yield of Ph–Ar^2 (%)[b]
1	F$_3$C, X (para)	3 3	97 (X = I) 95 (X = Br)
2	F$_3$C, Br (meta)	2	96
3	F, Br	2	95
4	O$_2$N, Br	4	87
5	Ac, Br	2	81
6	EtO$_2$C, Br	3 3	65 75[c]
7	NC, Br	3	69
8	OHC, Br	2 2	51 54[c]
9	MeO, Br	3 6	92 100[c]
10	methylenedioxy, Br	2	96
11	Et$_2$N, Br	5 3	75 88[d]
12	2-Me, Br	3	91
13	2-phenyl, Br	3	98
14	2,6-Me, Br	4	95
15	1-naphthyl, Br	3	96
16	2-bromopyridine	23	86
17	3-bromobenzothiophene	5	93

[a] Reactions were carried out using **1a** (1.1 mmol), an aryl bromide (1.0 mmol), PdCl$_2$ (0.05 mmol), PCy$_3$ (0.10 mmol) and TBAF·3H$_2$O (4.4 mmol) in DMSO–H$_2$O (10 : 1, 5.0 mL) at 80 °C. [b] Isolated yield based on aryl bromide. [c] DMSO–H$_2$O (2 : 1) was used as solvent. [d] DMSO–H$_2$O (20 : 1) was used as solvent.
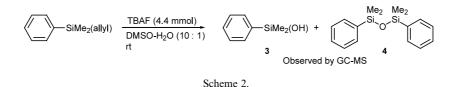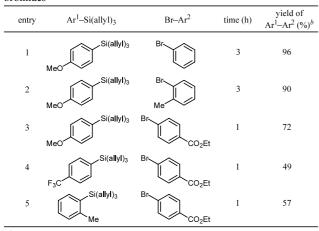
Scheme 2.

Table 2
Cross-coupling reaction of substituted triallyl(aryl)silane with aryl bromides [a]

entry	Ar^1–Si(allyl)$_3$	Br–Ar^2	time (h)	yield of Ar^1–Ar^2 (%)[b]
1	MeO—C$_6$H$_4$—Si(allyl)$_3$	Br—C$_6$H$_5$	3	96
2	MeO—C$_6$H$_4$—Si(allyl)$_3$	Br—C$_6$H$_4$—Me	3	90
3	MeO—C$_6$H$_4$—Si(allyl)$_3$	Br—C$_6$H$_4$—CO$_2$Et	1	72
4	F$_3$C—C$_6$H$_4$—Si(allyl)$_3$	Br—C$_6$H$_4$—CO$_2$Et	1	49
5	C$_6$H$_4$(Me)—Si(allyl)$_3$	Br—C$_6$H$_4$—CO$_2$Et	1	57

[a] Reactions were carried out using an arylsilane (1.1 mmol), an aryl bromide (1.0 mmol), PdCl$_2$ (0.05 mmol), PCy$_3$ (0.10 mmol) and TBAF·3H$_2$O (4.4 mmol) in DMSO–H$_2$O (10 : 1, 5.0 mL) at 80 °C. [b] Isolated yield based on aryl bromide.

Denmark have reported that arylsilanols are effective under different conditions [5].

In conclusion, we have demonstrated that triallyl(aryl)silanes are highly effective and convenient arylating reagents for the cross-coupling reaction with aryl bromides and iodides. The reaction tolerates a diverse range of functional groups. Stability and accessibility of the reagents compared with previous arylsilanes are worthy of note. Efforts to expand the scope of the present chemistry to aryl chlorides, other organic halides, and other organosilanes are ongoing subjects in our laboratory.

Acknowledgements

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[15] Although 1a tolerates treatment with 1 M NaOH aq. for a long period and brief treatment with 1 M HCl aq. does not affect, slow decomposition (ca. 20% conv.) was observed after 1 h treatment. The compound can be purified by flush chromatography on silica gel. See, also (a) R.A. Gossage, E. Muñoz-Martínez, G. van Koten, Tetrahedron Lett. 39 (1998) 2397; (b) X. Deng, A. Mayeux, C. Cai, J. Org. Chem. 67 (2002) 5279.
[16] Treatment of Ph–SiCl$_3$ with 3.3 equivalents of allylmagnesium bromide gives 1a (89% yield).
[17] General procedure: A mixture of triallyl(phenyl)silane (0.25 g, 1.10 mmol) TBAF·3H$_2$O (1.40 g, 4.40 mmol) in DMSO–H$_2$O (10:1, 5.0 ml) was degassed by three freeze–thaw cycles, and

stirred at room temperature for 1 h. To this were added PdCl$_2$ (8.9 mg, 50 µmol), PCy$_3$ (28 mg, 0.100 mmol) and 4-iodobenzotrifluoride (0.27 g, 1.00 mmol). The resulting mixture was stirred at 80 °C for 3 h before quenching with water, and the resulting mixture was extracted with Et$_2$O. Drying over MgSO$_4$, evaporation of the solvent, and purification by flash chromatography using silica gel afforded 4-trifluoromethylbiphenyl (0.22 g, 97%).

[18] Details of the results will be presented in a forthcoming full paper.

[19] Triallyl(aryl)silanes were prepared by sequential reaction of SiCl$_4$ with arylmagnesium bromide and allylmagnesium bromide. See, also Ref. [15].