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New Method for the Preparation of Functionalized Aryldiphenylsilanes ($ArPh_2SiH$)

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Abstract: Aryl halides are converted to aryldiphenylsilanes in moderate to good yields in the presence of tetraphenyldisilane and CsF in DMPU or HMPA. Ten examples are reported.
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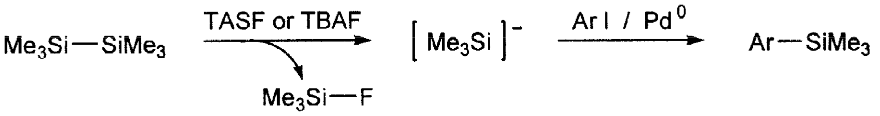
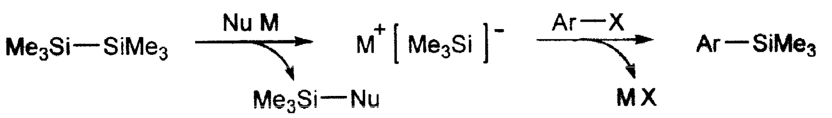
Organosilanes (R_3SiH) are used in organic chemistry as reducing agents[1] and occasionally for the protection of hydroxyl group.[2] Triarylsilanes (Ar_3SiH) are commonly prepared by the addition of organometallic reagents to chlorodiarylsilanes (Ar_2SiHCl) or diarylsilanes (Ar_2SiH_2).[3] This method has limited application since triarylsilanes, containing functional groups sensitive to organometallic reagents, are only accessible in multiple steps. The reduction of chlorotriarylsilanes (Ar_3SiCl) is another way to access triarylsilanes.[4] This approach requires the preparation of chlorotriarylsilanes, which are typically obtained by the addition of organometallic species to diaryldichlorosilanes (Ar_2SiCl_2)[5] or by the cross-coupling reaction between dichlorodisilanes ($R_2SiClSiClR_2$) and aryl halides catalyzed by a transition metal.[6] Both these approaches to chlorotriarylsilanes suffer limitations, the first one is limited for reasons previously mentioned and the second one, although more compatible with an array of functional groups, is limited by the low reactivity of dichlorodisilanes, high temperatures and long reaction times (140°C, 20h) are necessary for such cross-couplings to proceed.[6]

The nucleophilic silylation of aryl halides is a known procedure for the preparation of aryltrimethylsilanes[7] and aryltriphenylsilanes.[8] In particular, the formation of trimethylsilyl anion from hexamethyldisilane has been achieved in polar aprotic solvents (HMPT, HMPA or DMPU) using fluoride sources (TASF, TBAF) (equation 1)[7a] or *in situ* in the presence of aryl halides and reagents such as MeLi, MeONa and MeOK (equation 2).[7c] In the first example, the presence of a catalytic amount of Pd(0) is necessary for the reaction to proceed.



(1)



Nu M = MeLi, MeONa, MeOK
X = Br, Cl, I

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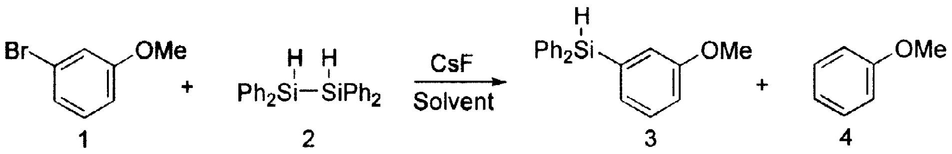
Inspired by these results, we hypothesized that generation of a silyl anion containing an Si-H bond should provide direct access to triarylsilanes (Ar_3SiH). After experimenting with various known methods, we found that addition of CsF to tetraphenyldisilane ($Ph_2SiHSiHPh_2$)[9] in polar aprotic solvents (HMPA, DMPU), produced a diphenylsilyl anion which reacted with 3-bromoanisole to give the desired diphenyl 3-methoxyphenylsilane in moderate to good yields (Table 1). In this communication, a new method for the preparation of aryldiphenylsilanes is reported.[10]

Cleavage of tetraphenyldisilane (1 eq.) with CsF (3 eq.) occurs readily (5 min) at room temperature in HMPA or DMPU to afford diphenylsilane (Ph_2SiH_2, 1 eq.) in quantitative yield, upon addition of water. The corresponding fluorodiphenylsilane was not detected. The silylation of 3-bromoanisole was found to proceed slowly at room temperature in HMPA or DMPU (Table 1, entries 2, 3 and 5). Running the reaction at higher temperature (100°C) dramatically increased the rate of silylation (Table 1, entries 4, 8). Improved yields were obtained by increasing the amount of CsF (Table 1, entries 6-8). In all cases the reduction of 3-bromoanisole to anisole was the main competitive side reaction. When the reaction was carried out in acetonitrile, only the reduction product was observed (Table 1, entry 1).

Table 1. Effect of Solvents, CsF and Temperature on the Reaction of 3-bromoanisole with Tetraphenyldisilane[a]

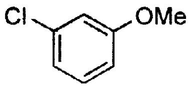
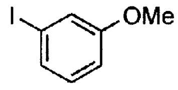
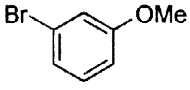
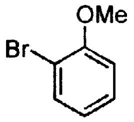
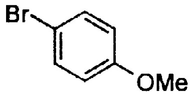
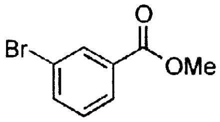
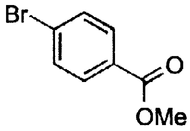
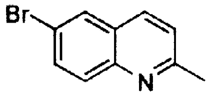
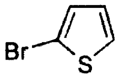
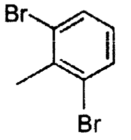


Entry	Solvent	CsF (eq.)	Temp. (°C)	Time	3^b (%)	4^b (%)	1^b (%)
1	CH_3CN	3.0	100	5 min	0	100	0
2	HMPA	3.0	25	4.5 hrs	12	5	82
3	HMPA	3.0	25	20 hrs	61	18	0
4	HMPA	3.0	100	5 min	61	17	3
5	DMPU	3.0	25	20 hrs	31	6	53
6	DMPU	0.5	100	5 min	34	10	53
7	DMPU	1.5	100	5 min	66	13	12
8	DMPU	3.0	100	5 min	74 (68)[c]	13	4

[a] 1.5 eq. of tetraphenyldisilane **2** were used. [b] Ratio (%) determined by ^1H NMR of the crude mixture after work-up ($NH_4Cl/CDCl_3$). [c] Isolated yield.

Having improved the reaction conditions, we investigated the reactivity of several aryl halides as summarized in Table 2. Aryl halides under the same conditions were found to give the best yield of desired material in the order Br > I > Cl (Table 2, entries 1-3). High level of reduction was observed for 3-iodoanisole (Table 2, entry 2). Surprisingly, the usually unreactive 3-chloroanisole afforded the desired arylsilane in moderate yield (Table 2, entry 1). The orientation of the electron donating methoxy group, in the ortho, meta or para positions had limited effect on the outcome of the silylation or the amount of reduced starting material (Table 2, entries 3-5). Similar results were observed for the electron withdrawing carboxylate ester, in the meta and para positions (Table 2, entries 6, 7). The preparation of diphenylsilyl benzoates (Table 2, entries 6, 7) from the corresponding aryl bromide in one step is an improvement over the currently known procedures that affords such compounds in multiple steps. Arylsilanes containing heterocyclic moieties are also accessible by this method (Table 2, entries 8, 9). Monosilylation of 2,6-dibromotoluene was accomplished in moderate yield (Table 2, entry 10) to afford a silane which could potentially be functionalized. For all aryl halides studied, the silylation occurred exclusively at the ipso position.

Table 2. Synthesis of Aryldiphenylsilanes

Entry	ArX	$ArSi(Ph)_2H^{a,b}$ (%)	ArH^a (%)	ArX^a (%)
1		43 (33)	9	45
2		51 (39)	35	3
3		74 (68)	13	4
4		83 (82)	13	0
5		60 (60)	21	0
6		58 (52)	15	7
7		65 (54)	22	2
8		54 $(48)^c$	32	0
9		(63)		
10		53 $(53)^d$		

[a] Ratio determined by ^1H NMR of the crude mixture after work-up with $NH_4Cl/CDCl_3$. [b] Isolated yields in parenthesis. [c] Reaction performed in HMPA. [d] Monosilylation product.

Work is currently underway to extend the scope of application of this method. Since triarylsilanes are known to be precursors for the silylation of hydroxyl groups, we believe that properly functionalized silanes may be used in combinatorial chemistry for the introduction of scaffolds connected on the polymeric support by a potential traceless silicon linker. In summary, the present method constitutes an improved route for the preparation of functionalized aryldiphenylsilanes.

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10. Typical Procedure: 600 μL of DMPU was added to tetraphenyldisilane (124 mg, 0.34 mmol) and flame dried CsF (103 mg, 0.68 mmol). To the resulting red suspension was added after 1 min 2-bromoanisole (41 mg, 0.22 mmol). The final mixture was rapidly heated at 100°C for 5 min in a closed vial. After cooling, the reaction mixture was poured in aqueous NH_4Cl (5%) and extracted three times with hexane. The organic extracts were combined, dried over $MgSO_4$, filtered and concentrated. Purification on preparative TLC (Hex/Tol, 4/1) afforded the desired material as a white solid (52 mg, 82%). m.p.:45°C. ^{1}H NMR (Acetone-d_6, 400 MHz) δ (ppm) 3.71 (s, 3H), 5.42 (s, 1H, Si-H), 6.95-7.03 (m, 2H), 7.33-7.49 (m, 8H), 7.56-7.59 (m, 4H). ^{13}C NMR (Acetone-d_6, 100 MHz) δ (ppm) 55.6, 111.1, 121.5, 122.3, 128.7, 130.2, 133.0, 134.8, 136.4, 138.2, 165.4. LRMS: (DCI; CH_4) m/z (relative intensity) 291 (MH+, 23), 289 (21), 214 (18), 213 (100). Anal. Calcd. for $C_{19}H_{18}OSi$: C, 78.57; H, 6.25. Found: C, 78.60; H, 6.41.