Efficient Synthesis of Substituted Diarylsilanes

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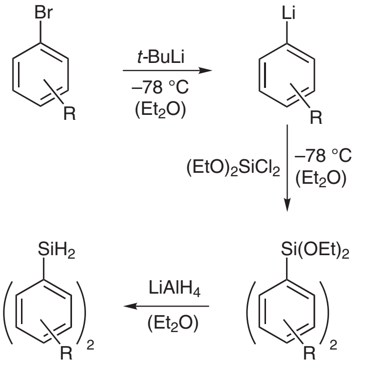
Abstract: A highly efficient synthesis of substituted diarylsilanes is presented. The treatment of substituted arylbromides with *tert*-butyllithium in diethyl ether at –78 °C, followed by the addition to dichlorodiethoxysilane at the same temperature, leads to the quantitative formation of diaryldiethoxysilane. Selective substitution of the chlorine atoms allows an aqueous work up in air. Subsequently, the diaryldiethoxysilane is reduced to the corresponding diarylsilane by stirring with lithium aluminum hydride in diethyl ether. The product is purified by bulb-to-bulb distillation. This method does not lead to any mono- or tri-substituted products and avoids handling gaseous and explosive dichlorosilane, which is a significant advantage over previously reported procedures.

Key words: arylation, hydrosilylation, lithiation, reduction, silicon

Secondary silanes are useful synthetic precursors for the preparation of silicon compounds such as chloro- and alkoxysilanes[1] or as precursors for dehydrocoupling reactions leading to oligo- and polysilanes.[2] Especially, diphenylsilane plays an important role in the hydrosilylation of ketones.[3] The use of substituted diarylsilanes allows the electronic and steric properties to be easily adjusted.[4] However, facile synthetic procedures with which to obtain diarylsilanes are still lacking.

One method involves handling gaseous and explosive dichlorosilane, which is reacted with Grignard reagents.[5] Others start from higher chloro- or ethoxysilanes, such as tetrachlorosilane,[6] trichlorosilane[7] or tetraethoxysilane.[8] The drawbacks of these methods are the concurrent formation of mono- and trisubstituted byproducts – if no sterically demanding substituent is used – and the resulting difficulties for the separation of the products. Furthermore, the residual chlorine substituents require anhydrous work-up.

In this work, a new, straightforward and generally applicable method with which to synthesize diarylsilanes, as depicted in Scheme 1, is reported. Dichlorodiethoxysilane was found to be the most appropriate precursor due to the differing reactivity of the Si–Cl and Si–O bonds. At –78 °C the chlorine atoms are selectively substituted by the aryllithium reagent, which is generated in situ, to form the diaryldiethoxysilane. After allowing the reaction mixture to warm to room temperature it was quenched with water, and processed through a simple work-up (see experimental section) to yield the diaryldiethoxysilane in nearly quantitative yield. In a second step, the ethoxy groups were reduced by lithium aluminum hydride in diethyl ether.[9]



Scheme 1 Synthesis of substituted diarylsilanes

After a straightforward work-up (see experimental section), the crude diarylsilane was purified by bulb-to-bulb distillation to afford the products in very good yields (see Table 1). The product purity was confirmed by NMR and infrared spectroscopy, and by elemental analysis.

This ease of access to substituted diaryldiethoxysilanes without formation of any mono- or trisubstituted species offers a number of further applications. Selected examples are presented in Figure 1.

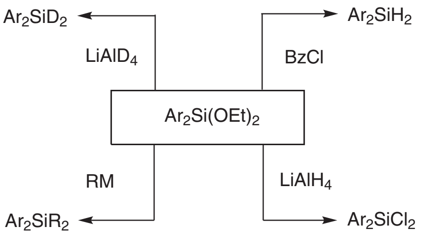


Figure 1 Important reactions involving diaryldiethoxysilanes

As mentioned above, the reduction of diaryldiethoxysilane with lithium aluminum hydride leads to the diarylsilane species.[9] The use of lithium aluminum deuteride instead, makes the corresponding deuterated diarylsilanes

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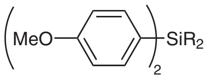
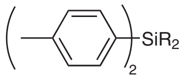
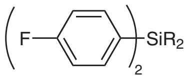
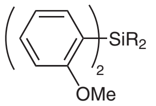
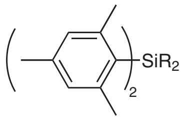
Table 1 Synthesized Diarylsilanes

Product	Yield (%)	
	R = OEt	R = H
	99	81
	98	78
	99	82
	96	74
	96	72

accessable.[10] Another possibility is to substitute the ethoxy groups with further alkyl or aryl substituents (R) to obtain quaternary silane species.[11] The reaction with benzoylchloride (Bz-Cl), yielding diaryldichloro species, offers further possibilities such as subsequent conversion into diarylalkoxysilanes or diaminodiarylsilanes.[12]

The presented method is a straightforward procedure with which to synthesize diarylsilanes in high yields. It avoids the use of gaseous dichlorosilane and prevents the formation of any byproducts, thus opening new and interesting applications in organosilicon chemistry.

All reactions were carried out under an anhydrous argon atmosphere using standard Schlenk techniques if not stated otherwise. Et_2O was dried by standard methods[13] and distilled under nitrogen. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL JMX-GX 400 MHz spectrometer at r.t. and calibrated using residual undeuterated solvent as an internal reference (benzene-d_6: $\delta = 7.15$ and 128.0 ppm, $CDCl_3$: $\delta = 7.26$ and 77.0 ppm). Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. IR spectra were acquired using a Jasco FT/IR-460 Plus spectrometer. Dichlorodiethoxysilane was purchased from ABCR and used without further purification.

Diethoxybis(4-methoxyphenyl)silane

At –78 °C, 4-bromoanisole (0.66 mL, 0.99 g, 5.29 mmol) was added dropwise to a solution of *t*-BuLi (1.9 M in pentane, 5.57 mL, 10.6 mmol) in anhydrous Et_2O (5 mL). The solution was stirred at this temperature for 2 h and then transferred to a pre-cooled solution of dichlorodiethoxysilane (0.44 mL, 0.50 g, 2.64 mmol) in Et_2O (5 mL) via cannula. The solution was stirred for 1 h at –78 °C and then allowed to warm to r.t. (**CARE**: gas evolution!). After quenching the reaction mixture with H_2O (8 mL), the phases were separated and the organic phase was washed with brine (5 mL), dried with Na_2SO_4, filtered and the solvent removed under vacuo.

Yield: 869 mg (99%); colorless oil.

^1H NMR (400 MHz, C_6D_6): $\delta = 1.21$ (t, $^3J = 7.1$ Hz, 6 H, CH_3), 3.27 (s, 6 H, OCH_3), 3.87 (q, $^3J = 7.1$ Hz, 4 H, CH_2), 6.87 (d, $^3J = 8.5$ Hz, 4 H, ArH), 7.83 (d, $^3J = 8.5$ Hz, 4 H, ArH).

^{13}C NMR (100 MHz, C_6D_6): $\delta = 18.6$ (s, CH_3), 54.5 (s, OCH_3), 58.8 (s, CH_2), 114.0 (s, Ar-C3/5), 125.2 (s, Ar-C1), 137.0 (s, Ar-C2/6), 161.9 (s, Ar-C4).

^{29}Si NMR (79 MHz, C_6D_6): $\delta = -30.4$ (s).

Di(4-methoxyphenyl)silane

Diethoxybis(4-methoxyphenyl)silane (869 mg, 2.61 mmol) was dissolved in anhydrous Et_2O (10 mL) and added dropwise to a suspension of LAH (198 mg, 5.23 mmol) in Et_2O (20 mL). The mixture was stirred for 16 h and then added to HCl (1 M, 15 mL). The organic phase was extracted with brine (10 mL), dried with Na_2SO_4, and filtered, before the solvent was removed in vacuo. The crude product was purified by bulb-to-bulb distillation (250 °C, 14 mbar) to afford the pure product.

Yield: 516 mg (81%); white solid.

IR (CH_2Cl_2): 2139 (Si–H) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.82$ (s, 6 H, OCH_3), 4.89 (s, 2 H, SiH), 6.93 (d, $^3J = 8.5$ Hz, 4 H, ArH), 7.52 (d, $^3J = 8.5$ Hz, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.0$ (s, OCH_3), 113.9 (s, Ar-C3/5), 122.6 (s, Ar-C1), 137.1 (s, Ar-C2/6), 161.1 (s, Ar-C4).

^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -34.0$ (s).

Anal. Calcd for $C_{14}H_{16}O_2Si$: C, 68.81; H, 6.60; Si, 11.49. Found: C, 68.78; H, 6.84; Si, 11.21.

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