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Rhodium(I)-Catalyzed Silylation of Aryl Halides with Triethoxysilane: Practical Synthetic Route to Aryltriethoxysilanes

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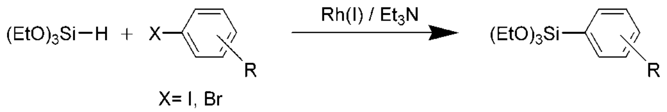
ABSTRACT



The specific silylation of aryl iodides and bromides with triethoxysilane $(EtO)_3SiH$ in the presence of NEt_3 and a catalytic amount of $[Rh(cod)(MeCN)_2]BF_4$ provides the corresponding aryltriethoxysilanes in high yield.

Hypervalent siloxane derivatives, which are obtained from aryl(trialkoxy)silanes and tetrabutylammonium fluoride, are versatile reagents for carbon−carbon[1−3] and carbon−heteroatom bond formation[4] and provide an alternative to the reaction of organotin or -boron compounds. Furthermore, considerable attention has recently been paid to rhodium-catalyzed addition of aryl(trialkoxy)silanes to carbonyl compounds, such as aldehydes,[5] α,β-unsaturated ketones, and esters.[5,6] Aryl(trialkoxy)silanes can be prepared by reacting aryl Grignard reagents with tetraalkyl orthosilicate, but it is difficult to prevent the formation of undesirable diarylsilanes.[1b,2,7]

Recently, we have developed the palladium(0)-catalyzed metalation of organic halides utilizing triethoxysilanes $(EtO)_3SiH$ (**1**)[8] or pinacolborane[9] as metalating reagents in the presence of tertiary amines. In the case of the silylation of aryl halides with **1** to provide aryl(triethoxy)silanes **3**, however, the electronic and steric characteristics of substrates have a significant impact on the reactions, i.e., the starting halides were restricted to aryl iodides having electron-donating groups at *para*-position.[8a] Very recently, the palladium(0)-catalyzed silylation has been extended to aryl bromides by DeShong, but the silylation of *ortho*-substituted or electron-deficient aryl halides was difficult by a similar limitation.[10] During the course of our studies, we found a new catalytic system for the silylation of aryl halides **2** with **1** (Scheme 1). We herein describe a rhodium(I)-catalyzed silylation of **2**, including aryl iodides and bromides having electron-withdrawing groups. Recently, Berry has reported

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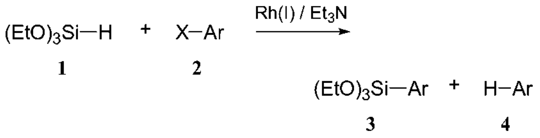
Scheme 1



$$\underset{\mathbf{1}}{(EtO)_3Si{-}H} + \underset{\mathbf{2}}{X{-}Ar} \xrightarrow{Rh(I)\,/\,Et_3N} \underset{\mathbf{3}}{(EtO)_3Si{-}Ar} + \underset{\mathbf{4}}{H{-}Ar}$$

on a rhodium-catalyzed dehydrogenative coupling of arenes and triethylsilane involving silylation of a carbon−halogen bond as a side reaction.[11] To our knowledge, however, there has been no report of rhodium-catalyzed silylation of organic halides using hydrosilane derivatives with high selectivity.

The reaction conditions were optimized using **1** (0.50 mmol) and ethyl 4-iodobenzoate (**2a**) (0.25 mmol), and the results are summarized in Table 1. As we reported recently, the palladium-catalyzed reaction of such an electron-deficient aryl iodide gave only 23% yield of the silylated product, ethyl 4-(triethoxysilyl)benzoate (**3a**), due to a strong tendency to produce the arene **4a**.[8] In the presence of a rhodium(I) catalyst (3 mol % of rhodium metal) and triethylamine (3 equiv), the reaction in DMF (1 mL) at 80 °C gave the desired arylsilane **3a** (76−88% yield) along with a small amount of a reduced byproduct **4a** (entries 1 and 2). The present silylation of **2a** was achieved with the aid of a tertiary amine analogous to the palladium-catalyzed silylation (entries 1, 2, and 4).[8,10] In the presence of other types of bases, the reactions occurred insufficiently (entries 5−7). Several solvents were tested (entries 8−11), and it was observed that the reaction in DMF afforded **3a** in acceptable yield.

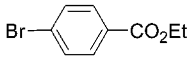
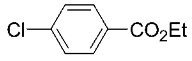
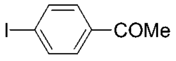
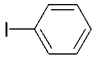
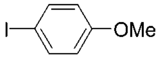
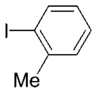
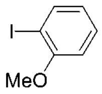
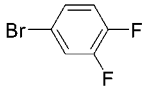
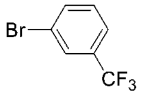
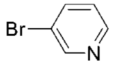
Table 1. Reaction of Ethyl 4-Iodobenzoate (**2a**) with Triethoxysilane (**1**) under Various Conditions[a]

				yield (%)[b]	
entry	catalyst	base	solvent	**3a**	**4a**
1	$[RhCl(cod)]_2$	Et_3N	DMF	76	16
2	$[Rh(cod)(MeCN)_2]BF_4$	Et_3N	DMF	88	12
3	$RhCl(PPh_3)_3$	Et_3N	DMF	15	35
4	$[RhCl(cod)]_2$	$^{i}Pr_2NEt$	DMF	75	15
5	$[RhCl(cod)]_2$	pyridine	DMF	0	6
6	$[RhCl(cod)]_2$	K_2CO_3	DMF	22	19
7	$[RhCl(cod)]_2$	KOAc	DMF	0	57
8	$[RhCl(cod)]_2$	Et_3N	NMP	30	46
9	$[RhCl(cod)]_2$	Et_3N	MeCN	28	17
10	$[RhCl(cod)]_2$	Et_3N	dioxane	0	20
11	$[RhCl(cod)]_2$	Et_3N	toluene	0	15

[a] Reactions of **2a** (0.25 mmol) with **1** (0.50 mmol) were carried out at 80 °C for 1 h in 1 mL of solvent by using a catalyst (3 mol % of rhodium metal) and a base (0.75 mmol). [b] GLC yields are based on **2a**.

The results obtained with representative aryl halides **2** are listed in Table 2. Under reaction condition similar to that used for the above silylation of **2a**, replacing the leaving group of aryl halides with the corresponding bromide **2b** gave lower yields of **3a** accompanied by a considerable amount of the arene **4a** (entry 1). We then examined a treatment with an additional equal amount of tetrabutylammonium iodide, and the silylation proceeded selectively (entries 2 and 9−11). The effect of iodide ion was unique to rhodium-catalyzed silylation, i.e., was not admitted in the palladium-catalyzed reaction,[10] suggesting another reaction process. Unfortunately, aryl chloride **2c** did not have enough reactivity and as a consequence **2c** was recovered (entry 3).

Table 2. Reaction of Representative Aryl Halides **2a**

entry	aryl halides **2**		time (h)	yield (%)[b]
1		(**2b**)	1	40
2[c]			1	90 (78[d])
3[c]		(**2c**)	16	9
4		(**2d**)	2	(75)
5		(**2e**)	2	(86[d])
6		(**2f**)	2	(90)
7		(**2g**)	2	(81)
8		(**2h**)	2	(87[d])
9[c]		(**2i**)	16	(76)
10[c]		(**2j**)	2	(70[d])
11[c]		(**2k**)	2	(80)

[a] All reactions were conducted in DMF (1 mL) at 80 °C using **2** (0.25 mmol) and **1** (0.50 mmol) in the presence of $[Rh(cod)(MeCN)_2]BF_4$ (0.0075 mmol) and Et_3N (0.75 mmol). [b] GLC yields are based on **2** used. Those in parentheses are isolated yields. [c] The reaction was performed in the presence of Bu_4NI (0.25 mmol). [d] The reaction was run on a 1.0 mmol scale.

The presence of functional groups, such as CO_2Et (entries 2 and 8) and COMe (entry 4), in the starting **2** did not interfere with the outcome of the present reaction at 80 °C. In contrast, the previous methods via Grignard reagents or organolithiums[7] require the protection of functional groups frequently. Also, the differences in the yields and on the selectivity among aryl halides **2** having electron-donating (entry 6) or -withdrawing groups (entries 2, 4, 9, and 10) were not particularly large. Then, sterically hindered **2g** and **2h** (entries 7 and 8) and heteroaromatic **2k** (entry 10) were also coupled with **1** without any difficulty. In contrast to the previous palladium-catalyzed silylation, both the yield and the selectivity are almost independent of the electronic

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and steric requirement. Particularly, the present results are the first examples of the silylation of *ortho*-substituted or electron-deficient aryl halides. As a whole, the desired products **3** were contaminated with small amounts of the reduced byproducts **4**, but their isolation was very easy. Accordingly, the present reaction provides a simple and widely available procedure for synthesizing aryl(triethoxy)silanes **3**.

A plausible reaction pathway is shown in Figure 1, although there is no clear experimental evidence. Initially, triethoxysilanes **1** would add to the rhodium(I) catalyst to give a silyl hydrido species, **5**,[12] followed by reductive elimination of hydrogen halide HX with the aid of triethylamine, giving a silyl rhodium(I) complex, **6**.[13] Then, oxidative addition of the aryl halide **2** would furnish an arylrhodium(III) intermediate, **7**, and subsequent reductive elimination would lead to the product **3** along with regeneration of the catalyst. Hydrogenolysis of **2**, affording a reduced byproduct, **4**, would occur in the case that reductive elimination of halosilane $(EtO)_3SiX$ from **5** or **7** proceeded. Bearing in mind the previously described result, in which iodosilane added oxidatively to a transition metal in the presence of triethylamine,[14] silyl(hydrido)-rhodium(III) iodide (**5**, X = I) may be more favorable for preventing reductive elimination of halosilane. The effect of iodide ion on the reaction of aryl bromide can be understood in terms of the ligand exchange between iodide ion and X of the rhodium(III) halide **5** or **7**.

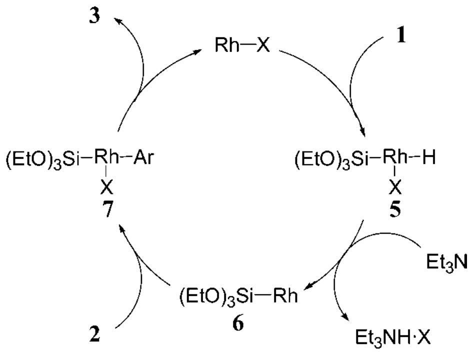

Figure 1. Plausible catalytic cycle for silylation of **2**.

In conclusion, the rhodium(I) complex is an the effective catalyst for the silylation of a wide range of aryl halides **2** utilizing triethoxysilane **1** as silylating reagents in the presence of a tertiary amine. Investigations for circumstantial mechanistic studies and silylations of other organic halides are currently in progress in our laboratory.

Supporting Information Available: Experimental procedures and spectroscopic data. The material is available free of charge via the Internet at http://pubs.acs.org.

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