Rhodium(I)-Catalyzed Synthesis of Aryltriethoxysilanes from Arenediazonium Tosylate Salts with Triethoxysilane

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Abstract: An efficient method for the preparation of aryltriethoxysilanes from arenediazonium tosylate salts has been developed, which expands the substrates of rhodium-catalyzed silylation from iodides, bromides, and triflates to diazonium salts. A new method for hydrodediazoniation has also been explored.

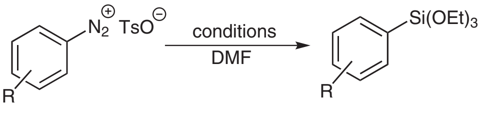
Key words: silylation, diazo compounds, aryltriethoxysilane, rhodium catalyst, arenes

As versatile reagents[1–6] for carbon–carbon and carbon–heteroatom bond formation, arylsiloxanes are widely employed in the metal-catalyzed cross-coupling reactions (e.g., Hiyama coupling[6]) for the synthesis of unsymmetrical biaryl derivatives and substituted alkenes. The most common method for the synthesis of arylsiloxanes is based on the reactions of tetraalkyl orthosilicate with Grignard[6b] or lithium[7] reagents. These metalloid reactions generally suffer from inferior yields during the preparation of siloxanes and difficulties in synthesizing arylmetalloids having electrophilic functional groups (i.e., esters, ketones, etc.). In order to overcome these drawbacks, Murata[8–10] and DeShong[11] have developed new approaches for the synthesis of aryltriethoxysilanes using transition-metal-catalyzed (palladium or rhodium) metalation of aryl halides or aryl triflate esters with triethoxysilanes $HSi(OEt)_3$. The rhodium(I)-catalyzed silylation has been optimized to occur in mild conditions, and the substrates has been expanded from aryl iodides to aryl bromides, triflates, and nonaflates.[10] However, there are still some limitations remained to be solved. For example, aromatic amino groups are widely used for positional control in many electrophilic substitutions and coupling reactions.[12] Further transformation of aromatic amino groups is, therefore, often necessary. Accordingly, the goal of this study is to extend the rhodium(I)-catalyzed silylation reaction to achieve further transformations of arylamine substrates. Meanwhile, a new method for removal of amino groups via hydrodediazoniation is also explored during the course of our research.

At first, we focused on the silylation reaction with arenediazonium tetrafluoroborate salts because they can be easily prepared from arylamines in high yields.[13–18] Additionally, the arenediazonium salts are more reactive than the corresponding aryl halides and triflates.[19–21] The rhodium(I)-catalyzed silylation of arenediazonium tetrafluoroborate salts was performed in one-pot as described by Murata[10] and Deshong.[11] However, our GC-MS results showed that, instead of the desired aryltriethoxysilane, hydrodediazoniation product occurred exclusively (Table 1, entry 1). We suspected that the presence of fluorinated groups might interfere with the silylation. In order to demonstrate this, an equivalent amount of sodium tetrafluoroborate was added to the reaction system with 1-iodo-4-methyl-benzene as the starting material (Table 1, entry 3). Similar to the result obtained with arenediazonium tetrafluoroborate salts, GC-MS results showed no evidence for the formation of any siloxane compounds. By contrast, triethoxysilane product occurred in good yield when an equivalent amount of sodium tosylate was added instead (Table 1, entry 4).

We, therefore, started out to employ the rhodium(I)-catalyzed silylation with arenediazonium tosylate salts (Scheme 1). Filimonov reported very recently a facile method for the preparation of pure arenediazonium tosylate salts from arylamines.[22] Various arenediazonium tosylate salts were accordingly prepared in our laboratory under modified reaction conditions by replacement of the reported AcOH/Resin NO_2^- with *t*-BuONO–THF.[23] The expected silylation reaction of arenediazonium tosylate salt took place with a moderate yield of the desired aryltriethoxylsilane after heating at 80 °C for one hour (Table 1, entry 5). However, considerable amount of hydrodediazoniation product was formed simultaneously in a competing side reaction. Fortunately, when changing the feeding sequence to optimize the reaction conditions, the aryltriethoxylsilane product was obtained in a good yield (Table 1, entry 6).

Our results obtained for the rhodium(I)-catalyzed silylation with representative diazonium tosylate salts were summarized in Table 2. All experiments were performed in the presence of 1.0 equivalent of Bu_4NI and 0.05 equivalent of rhodium(I) catalyst (Scheme 1). Other reagents



Scheme 1 *Reagents and conditions*: $[Rh(cod)Cl]_2$, Et_3N, Bu_4NI, DMF, r.t., 2 h, then $HSi(OEt)_3$, reflux, 8 h.

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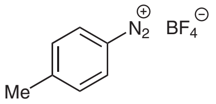
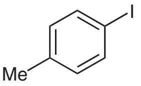
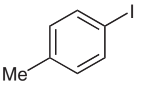
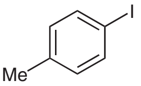
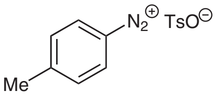
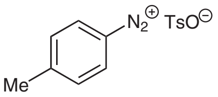
Table 1 Selected Contrasting Reactions

Entry	Starting material	Conditions	Yield (%)[a]
1		$[\mathrm{Rh(cod)Cl}]_2$, $\mathrm{Et_3N}$, $\mathrm{Bu_4NI}$, DMF, $\mathrm{HSi(OEt)_3}$, reflux, 8 h	0[b]
2		$[\mathrm{Rh(cod)Cl}]_2$, $\mathrm{Et_3N}$, DMF, $\mathrm{HSi(OEt)_3}$, reflux, 8 h	88
3		$\mathrm{NaBF_4}$, $[\mathrm{Rh(cod)Cl}]_2$, $\mathrm{Et_3N}$, DMF, $\mathrm{HSi(OEt)_3}$, reflux, 8 h	0[b]
4		NaTsO, $[\mathrm{Rh(cod)Cl}]_2$, $\mathrm{Et_3N}$, DMF, $\mathrm{HSi(OEt)_3}$, reflux, 8 h	89
5		$[\mathrm{Rh(cod)Cl}]_2$, $\mathrm{Et_3N}$, $\mathrm{Bu_4NI}$, DMF, $\mathrm{HSi(OEt)_3}$, reflux, 1 h	41
6		(1) $[\mathrm{Rh(cod)Cl}]_2$, $\mathrm{Et_3N}$, $\mathrm{Bu_4NI}$, DMF, r.t., 2 h; (2) $\mathrm{HSi(OEt)_3}$, reflux, 8 h	88

[a] Isolated yields of the silylation product (4-tolyltriethoxysilane) after silica gel column chromatography.

[b] Yields based on the GC-MS analysis. However, the hydrodediazoniation product (toluene) was obtained exclusively.

were added according to the protocol reported by Murata.[8–10] For most substrates, the desired products, that is, aryltriethoxysilanes, were obtained in good yields after isolation by silica gel column chromatography. In comparison with the methods via Grignard reagent or lithium reagent which are inapplicable to arylamines attaching some functional groups (e.g., COMe and $\mathrm{CO_2Me}$), this rhodium-catalyzed silylation reaction showed remarkable advantages (Table 2, entries 5 and 6). Moreover, the diazonium tosylate salts with electron-donating or -withdrawing groups both gave good product yields (Table 2).

We proposed that two successive reactions might take place in the one-pot procedure. When diazonium salts were treated with an equivalent of tetrabutylammonium iodide, a quantitative Sandmeyer reaction proceeded to give the corresponding products via nucleophilic replacement.[22] Triethoxysilane was then added to carry out the silylation via a typical procedure.[24] For the substrate with *ortho*-substituted groups, the desired reaction failed to occur (Table 2, entry 7). GC-MS investigation on the reaction mixture indicated that the first Sandmeyer reaction did not proceed completely, which prevented further transformation to the aryltriethoxylsilane product. For the arylamines with strong electron-withdrawing groups, the silylation did not proceed (Table 2, entries 8 and 10).

Table 2 Silylation of Arenediazonium Tosylate Salts[a]

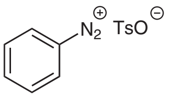
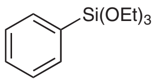
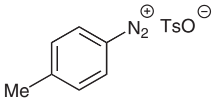
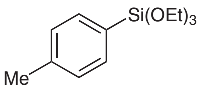
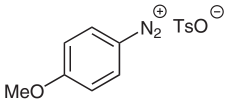
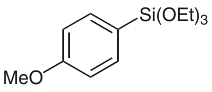
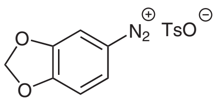
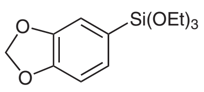
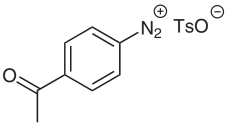
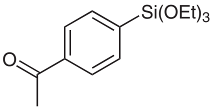
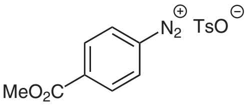
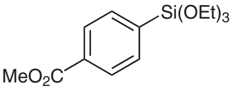
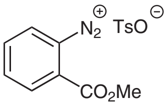
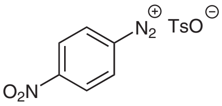
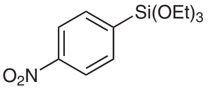
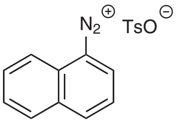
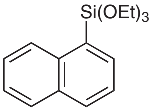
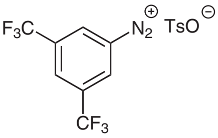
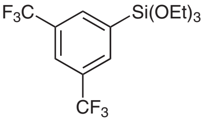
Entry	Starting material	Product	Yield (%)
1			85
2			89
3			90
4			88

Table 2 Silylation of Arenediazonium Tosylate Salts[a] (continued)

Entry	Starting material	Product	Yield (%)
5			76
6			85
7		–	0[b]
8			0
9			86
10			0

[a] The reaction conditions are listed in Scheme 1. The yields of silylation products are isolated yields after silica gel column chromatography.

[b] The desired silylation product was not obtained. Methyl benzoate was obtained in 91% yield instead.

Scheme 2 *Reagents and conditions*: $[Rh(cod)Cl]_2$, $HSi(OEt)_3$, DMF, r.t., 2 h.

Meanwhile, we found that the rhodium(I) catalyst together with $HSi(OEt)_3$ could smoothly reduce the arenediazonium tetrafluoroborate salts to arenes in high yields, which showed a potential application for hydrodediazoniation (Scheme 2). The representative results are listed in Table 3. Although numerous organic[25] and inorganic[26–31] reagents have been employed to realize the hydrodediazoniation reaction, our method using triethoxysilane turned out to have unique advantages, especially for those reactions performed under anhydrous conditions.[32]

In conclusion, we have explored an efficient rhodium(I)-catalyzed method for silylation of arenediazonium tosylate salts, which has extended the scopes of substrates from aryl halides and triflates to arylamines. By this means, a wide range of substituted arylamines could be converted into aryltriethoxysilanes, complex functional siloxanes, and other silicon materials in practical synthesis. In addition, a new method for hydrodediazoniation of arenediazonium tetrafluoroborate salts has been developed, which is general and mild for use.

Table 3 Hydrodediazoniation of Diazonium Tetrafluoroborate Salts

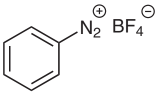
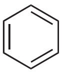
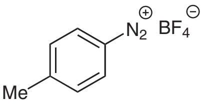
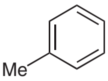
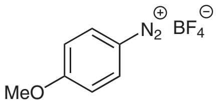
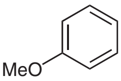
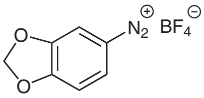
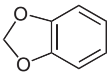
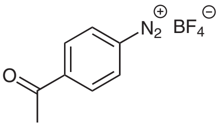
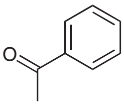
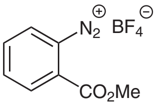
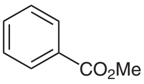
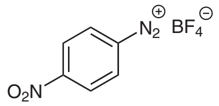
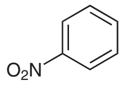
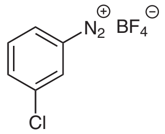
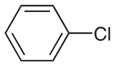
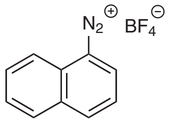
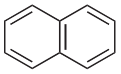
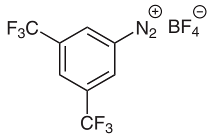
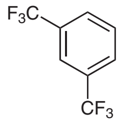
Entry	Starting material	Product	Yield (%)
1			95[a]
2			94[a]
3			94[a]
4			94[a]
5			93[a] (85[b])
6			95[a]

Table 3 Hydrodediazoniation of Diazonium Tetrafluoroborate Salts (continued)

Entry	Starting material	Product	Yield (%)
7			95[a] (89[b])
8			93[a]
9			90[b]
10			91[a]

[a] Yields based on the GC-MS analysis.

[b] Isolated yields after silica gel column chromatography.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(23) **Typical Method for the Preparation of Arenediazonium Tosylate Salts**

To a solution of methyl 4-aminobenzoate (1.0 mmol) in THF (5 mL) and AcOH (5 mL) was added PTSA·H_2O (1.1 mmol). Immediately, pale solids were precipitated. About 8 mL of AcOH was added until the solution turned clear again. The solution was then cooled to –10 °C, and then *t*-BuONO (1.5 mmol) was added dropwise to the reaction. The mixture was stirred for 30 min and then warmed to r.t. for another 30 min. The clear solution was poured into Et_2O (100 mL), and the diazonium tosylate salt was precipitated. After careful filtration, the product was collected to give a yield of 91%.

4-Methoxycarbonylbenzenediazonium Tosylate

IR (neat): 3566, 3483, 3101, 2311, 1723, 1438, 1302, 1195, 1122, 1036, 1009, 865, 817, 763, 684, 568, 525 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 2.27$ (s, 3 H), 3.95 (s, 3 H), 7.09 (d, 2 H, $J = 8.0$ Hz), 7.46 (d, 2 H, $J = 8.0$ Hz), 8.39–8.43 (m, 2 H), 8.78–8.80 (m, 2 H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 20.86$, 51.68, 115.41, 120.34, 125.59, 128.24, 131.47, 138.03, 145.30, 162.04, 166.13 ppm. MS (ESI): *m/z* = 163 [M^+], 162.9.

(24) **Typical Procedure for the Silylation**

Toluenediazonium tosylate salt (280 mg, 1.0 mmol, and Bu_4NI (369 mg, 1.0 mmol) were placed in a 25 mL of three-necked flask which was capped with septum rubbers. The flask was evacuated and backfilled with argon, and then charged with DMF (4 mL), Et_3N (3.0 mmol), and chloro(1,5-cyclooctadiene) rhodium(I) dimer (5 mol%, 0.05 mmol). The reaction mixture was stirred for 2 h at r.t. Triethoxysilane (2.0 mmol) was added by a syringe through the septum rubber. The reaction mixture was then stirred at 80–100 °C. After the reaction, the mixture was diluted with Et_2O, washed three times with H_2O to remove DMF, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by Kugelrohr distillation or silica gel column to give the desired 4-tolyltriethoxysilane 223 mg, yield 89%.

IR (neat): 2975, 2926, 2887, 1656, 1630, 1444, 1391, 1295, 1167, 1127, 1103, 1080, 959, 781, 712, 505 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (t, 9 H, $J = 7.2$ Hz), 2.38 (s, 3 H), 3.91 (q, 6 H, $J = 7.2$ Hz), 7.23 (d, 2 H, $J = 8.0$ Hz), 7.63 (d, 2 H, $J = 8.0$ Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 17.86, 21.20, 58.33, 127.81, 128.38, 134.59, 139.91 ppm. MS (EI): *m/z* = 254 [M^+], 254, 209, 195, 181, 162, 147, 139, 119, 91, 45.

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(32) **General Procedure for the Hydrodediazoniation**
To a solution of arenediazonium tetrafluoroborate (1.0 mmol) in anhyd DMF (2 mL), was added catalytic amount (0.0005 mmol) of chloro(1,5-cyclooctadiene) rhodium(I) dimer at r.t. Then triethoxysilane (1 equiv, 164 mg, 1.0 mmol) was added to the solution in one portion. Lots of gas escaped rapidly and the yellow-color reaction mixture turned into dark and green. The reaction was allowed to stir at r.t. for 30 min. After no nitrogen bumbled, the mixture was extracted with Et_2O and washed many times with H_2O to remove the DMF as much as possible. The crude product was purified with silica gel column or identified by GC-MS to obtain the required arene with yields from 85–95%.