



Short communication

Rhodium-catalyzed arylation of acylsilanes with sodium tetraarylborates



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ABSTRACT

Rhodium(I)-catalyzed arylation of benzoylsilanes with sodium tetraarylborates affords α -silyl benzhydrols, benzhydryl silyl ethers, benzhydrols, and diaryl ketones selectively depending on the catalyst, solvent, and temperature.

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Introduction

Extensive studies have been conducted on rhodium(I)-catalyzed 1,2-addition reactions of arylboron compounds to carbonyl compounds, which has become an indispensable synthetic tool in the preparation of alcohols and ketones [1]. Several classes of carbonyl compounds, including aldehydes [2], ketones [3], esters [4] and acid anhydrides [5], have been identified as viable reaction partners for the rhodium(I)-catalyzed arylation with arylboron compounds. However, to the best of our knowledge, the literature contains no reports of the rhodium(I)-catalyzed arylation of acylsilanes with arylboron compounds [6,7]. We herein report that rhodium-catalyzed addition reactions of sodium tetraarylborates to acylsilanes yield distinct arylation products depending on the reaction conditions employed.

Results and discussion

We began our investigation with the rhodium-catalyzed arylation of benzoyltrimethylsilane (**1a**). When benzoylsilane **1a** was reacted with sodium tetraphenylborate (**2a**) in toluene at 90 °C in

the presence of a catalytic amount of $[\text{Rh}(\text{OH})(\text{cod})]_2$ (cod = cycloocta-1,5-diene), 1,2-addition of arylrhodium(I) species to the carbonyl group of **1a** occurred to give diphenyl(trimethylsilyl)methanol (**3aa**) in 68% yield (Table 1, entry 1) [8–10]. The carbonyl arylation is considered to proceed via 1,2-addition of an arylrhodium(I) species to an acylsilane C=O bond. Other tetraarylborates **2b–e** also participated in the reaction with **1a** to produce the corresponding α -silyl benzhydrols **3ab–ae** (entries 2–5). Product **3af** derived from electron-rich tetraarylborate **2af** (Ar = 4-MeOC₆H₄) was unstable, and it rearranged to diaryl ketone **6f** during isolation (entry 6) [11]. The half-life for the rearrangement of relatively stable **3ad** (Ar = 4-CF₃C₆H₄) was determined by ¹H NMR to be approximately two weeks at room temperature in the absence of light [12]. Benzoylsilanes bearing SiMe₂Ph and SiMe₂*t*-Bu groups were also converted to the corresponding α -silyl benzhydrols (**3ba** and **3ca**), albeit with reduced efficacy (entries 7 and 8). In cases where $[\text{RhCl}(\text{cod})]_2$ was used as a catalyst instead of $[\text{Rh}(\text{OH})(\text{cod})]_2$, a decrease in yields was observed (**3aa**: 52%, **3ba**: 44%, **3ca**: 42%).

In addition to the benzoylsilanes **1a–c**, acetyl(trimethylsilyl)silane (**1d**) was also utilized as the substrate for the rhodium-catalyzed arylation with **2** (Scheme 1). The reaction of **1d** and **2a** furnished 1-phenyl-1-silylethanol **3da** in 60% yield.

In contrast, the reaction performed in 1,4-dioxane in the presence of $[\text{RhCl}(\text{cod})]_2$ provided benzhydryl trimethylsilyl ether (**4aa**) in 81% NMR yield (Scheme 2). The silyl ether **4aa** was desilylated

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Table 1
Rhodium-catalyzed arylation of benzoyltrimethylsilane to afford α -silyl benzhydrols **3**.^a

Entry	1 (Si)	2 (Ar)	Product	Yield (%)
1	1a (SiMe ₃)	2a (Ph)	3aa	68 ^b (65) ^c
2	1a	2b (4-MeC ₆ H ₄)	3ab	56
3	1a	2c (3-MeC ₆ H ₄)	3ac	46
4	1a	2d (4-CF ₃ C ₆ H ₄)	3ad	60
5	1a	2e (4-ClC ₆ H ₄)	3ae	52
6	1a	2f (4-MeOC ₆ H ₄)	3af	— ^d
7	1b (SiMe ₂ Ph)	2a	3ba	53 ^e
8	1c (SiMe ₂ <i>t</i> -Bu)	2a	3ca	52 ^f

^a Conditions: **1** (0.10 mmol), **2** (0.15 mmol), and [Rh(OH)(cod)]₂ (3.0 μmol, 6 mol% Rh) in toluene (1.0 mL) at 90 °C for 8 h.

^b 52% yield with [RhCl(cod)]₂.

^c Performed on a 0.5 mmol scale.

^d Diaryl ketone **6f** was isolated in 46% yield.

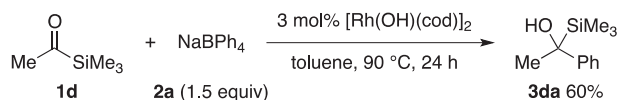
^e 44% yield with [RhCl(cod)]₂.

^f 42% yield with [RhCl(cod)]₂.

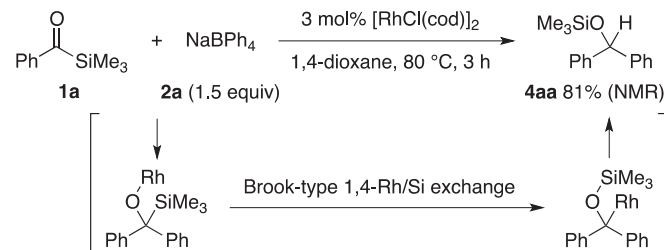
during chromatography over silica gel to afford benzhydrol (**5a**) in 59% yield. The formation of **4aa** can be accounted for by considering the Brook-type 1,4-rhodium/silicon exchange occurring with the intermediate [diphenyl(trimethylsilyl)methoxy]rhodium(I) [13–15]. Similar results were obtained when the reaction was performed in the absence of light (**4aa**, 53% NMR yield), indicating that siloxycarbene generated by a photoinduced 1,2-silyl shift might not be involved in the process.

The reaction performed in protic solvents led to the exclusive formation of desilylated benzhydrols **5** (Table 2). The arylation of **1a** with **2a** in EtOH in the presence of [RhCl(cod)]₂ produced alcohol **5a** in 73% yield. Because **3aa** was recovered unchanged when heated at 90 °C in EtOH both in the presence and absence of the rhodium catalyst, the formation of **5a** may be ascribed to the desilylation of **4aa** instead of **3aa** under these catalytic conditions. Phenyl(tolyl)methanols (**5b** and **5c**) were obtained from the reaction of **1a** with tolylborates (**2b** and **2c**) (entries 2 and 3). Although borates **2d** and **2e** failed to give benzhydrols **5**, 4-methoxyphenyl derivative **2f** was successfully arylated with **1a** to afford **5f** in 61% yield (entry 4). The use of dimethyl(phenyl)silyl derivative **1b** for the reaction with **2a** also led to the formation of desired product **5a** in 83% yield (entry 5), whereas the reaction of **1c** produced TBS ether **4ca**, which was resistant to desilylation under the investigated reaction conditions (entry 6).

The rhodium-catalyzed arylation of **1** under more forcing conditions gave rise to diaryl ketones **6** (Table 3) [16,17]. Because the oxidation of alcohols **5** to ketone **6** under the investigated reaction conditions was virtually unnoticeable, **6** appears to be formed directly from α -silyl benzhydrols **3**. Indeed, heating **3aa** at 130 °C in *p*-xylene for 24 h, irrespective of the presence of the rhodium catalyst, resulted in the formation of **6a** (49% yield without Rh; 28% yield with Rh), in contrast to the inertness of **3** in solution at temperatures less than 90 °C (*vide supra*).



Scheme 1. Arylation of acetylsilane **1d** with **2a**.



Scheme 2. Rhodium-catalyzed arylation of **1a** affording benzhydryl silyl ether **4**.

Table 2
Rhodium-catalyzed arylation of **1** to afford benzhydrols **5**.^a

Entry	1 (Si)	2 (Ar)	Product	Yield (%)
1	1a (SiMe ₃)	2a (Ph)	5a	73 (84) ^b
2	1a	2b (4-MeC ₆ H ₄)	5b	87
3	1a	2c (3-MeC ₆ H ₄)	5c	42
4	1a	2f (4-MeOC ₆ H ₄)	5f	61
5	1b (SiMe ₂ Ph)	2a	5a	83
6	1c (SiMe ₂ <i>t</i> -Bu)	2a ^c	4ca ^d	50 ^e

^a Conditions: **1** (0.10 mmol), **2** (0.15 mmol), and [RhCl(cod)]₂ (3.0 μmol, 6 mol% Rh) in EtOH (1.0 mL) at 90 °C for 16 h.

^b Performed on a 0.5 mmol scale (14 h).

^c 1.5 equiv of **2a** was used.

^d Benzhydryl *tert*-butyldimethylsilyl ether.

^e 69% yield with 3 equiv of **2a**.

Conclusion

In summary, the addition of sodium tetraarylbates **2** to acylsilanes **1** occurred in the presence of rhodium(I) catalysts. The reaction gave α -silyl benzhydrols **3**, benzhydryl silyl ethers **4**, benzhydrols **5**, and diaryl ketones **6** depending on the conditions employed (Scheme 3). Alcohols **5** and ketones **6** were derived only from silyl ethers **4** and silyl alcohols **3**, respectively.

Table 3
Rhodium-catalyzed arylation of **1** to afford diaryl ketones **6**.^a

Entry	1 (Si)	2 (Ar)	Product	Yield (%)
1	1a (SiMe ₃)	2a (Ph)	6a	67 (73) ^b
2	1a	2b (4-MeC ₆ H ₄)	6b	47
3	1a	2c (3-MeC ₆ H ₄)	6c	55 ^c
4	1a	2d (4-CF ₃ C ₆ H ₄)	6d	53
5	1a	2e (4-ClC ₆ H ₄)	6e	40
6	1a	2f (4-MeOC ₆ H ₄)	6f	39 ^c
7	1b (SiMe ₂ Ph)	2a ^d	6a	68
8	1c (SiMe ₂ <i>t</i> -Bu)	2a ^d	6a	36 ^e

^a Conditions: **1** (0.10 mmol), **2** (0.15 mmol), and [RhCl(cod)]₂ (3.0 μmol, 6 mol% Rh) in *p*-xylene (1.0 mL) at 130 °C for 24 h.

^b Performed on a 0.5 mmol scale (45 h).

^c Determined by ¹H NMR.

^d 1.5 equiv of **2a** was used.

^e 46% yield with 3.0 equiv of **2a**.

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