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Rhodium(I)-Catalyzed 1,2- and 1,4-Addition of Aryltriethoxysilanes to Carbonyl Compounds under Basic Aqueous Conditions

Miki Murata,* Ryuta Shimazaki, Masanori Ishikura, Shinji Watanabe, and Yuzuru Masuda*

Address: Department of Materials Science, Kitami Institute of Technology,
Kitami, 090-8507, Japan

Fax: +81-157-26-4973

E-mail: muratamk@mail.kitami-it.ac.jp, masudayz@mail.kitami-it.ac.jp

Abstract

Aryltriethoxysilanes were added to aldehydes and α,β -unsaturated carbonyl compounds in high yield in the presence of a rhodium(I) catalyst and aqueous sodium hydroxide.

Keywords: Rhodium, Addition reactions, Silicon, Arylations, Carbonyl compounds

Hypervalent siloxane derivatives, which are obtained from aryl(trialkoxy)silanes and tetrabutylammonium fluoride, are versatile reagents for carbon-carbon and carbon-heteroatom bond formation, and provide an alternative to the reaction of organotin or -boron compounds. The palladium-catalyzed cross-coupling reaction with organic electrophile¹ and the copper-mediated amination reaction² should proceed through a transmetalation to transition metals. We have recently reported on a practical example of a palladium-catalyzed cross-coupling reaction of aryltriethoxysilanes **1** with aryl bromides in the presence of an aqueous base.³ The aqueous base as well as fluoride ion will promote the transmetalation between **1** and a transition metal complex.

In this paper, we describe a rhodium-catalyzed addition of **1** to aldehydes **2** under aqueous basic condition (Scheme 1). The rhodium-catalyzed 1,2- and 1,4-additions of

organometallic reagents, such as organotin⁴ and -boron⁵ reagents, to carbonyl compounds have been recognized useful methods for carbon-carbon bond formation, and the transmetalation between such organometallic reagents and a rhodium complex has been proposed as a key step of the catalytic cycle.

<<Scheme 1>>

Very recently, the 1,2-additions of arylsilanes, such as halosilanes⁶ and silandiols,⁷ have been investigated. Also, the conjugated additions of these, such as halosilanes,⁸ silandiols,⁹ and methoxysilanes,¹⁰ have been reported. In comparison with other silicon reagents, aryltriethoxysilanes **1** should have greater advantages of the availability; i.e., several synthetic routes to **1** have been developed, e.g. the palladium-catalyzed silylation of organic halides utilizing triethoxysilane¹¹ and the reaction of Grignard reagents with tetraethyl orthosilicate.³ Therefore, the present addition of **1** should provide a synthetically useful and alternative method.

<<Table 1>>

A series of reactions of phenyltriethoxysilane **1a** (0.50 mmol) with benzaldehyde **2a** (0.25 mmol) were performed under several conditions for optimization studies (Table 1). In the presence of a rhodium(I) μ -hydroxo complex (0.0038 mmol),¹² 1,5-cyclooctadiene (0.075 mmol), and aqueous sodium hydroxide (0.25 mmol), the reaction in dioxane (1 ml) at 90 °C gave the desired benzhydrol **3a** in a 79% yield (entry 1). Although commercially available μ -chloro and cationic complexes were also effective as for the catalyst (entries 3 and 4), an additional 1,5-cyclooctadiene as a ligand was necessary to any rhodium catalyst, since the use of rhodium complex alone resulted in low yield due to the catalyst decomposition during the reaction (entry 2). The present addition was achieved with the aid of an aqueous solution of hydroxide ion analogous to the palladium-catalyzed cross-coupling reaction;³ i.e., the reactions of **1a** occurred insufficiently in the presence of fluoride ion (entries 7 and 8)⁶ or in the absence of a base (entry 5),⁷ even though the cited additions of arylsilanes have been reported. Several solvents including DMF and toluene were tested, and it was observed that the reaction in ether solvents afforded **3a** in acceptable yield (entries 10 and 11).

Generally, the role of negatively charged bases, such as fluoride and hydroxide ion, on the transition metal-catalyzed reaction of organosilanes is recognized to be the increase of its nucleophilicity due to the coordination of the base to the silicon atom.¹⁴ Although there is no clear experimental evidence, we speculated that the present addition involved the transmetalation between a rhodium complex and the hypervalent siloxanes, which was obtained from aryltriethoxysilanes **1** and aqueous sodium hydroxide.

<<Table 2>>

The results obtained with representative arylsilanes **1** and aldehydes **2**, which gave the product **3** in a similar manner to the above, are listed in Table 2. In the presence of aqueous sodium hydroxide, aryltriethoxysilanes **1** were more efficient arylating substances; i.e., replacing the arylating agent with other silicon compounds gave lower yields of **3** (entries 1-4). The differences in the yields among electronic characteristics of the substituent on **1** were not particularly large (entries 5 and 6). Although **1** added to **2** having the electron-withdrawing group without any difficulty (entry 7), the reaction of electron-rich aldehydes required more amount of 1,5-cyclooctadiene as a ligand and/or more elevated temperature (entries 8 and 9).

Finally, results for the 1,4-addition of aryltriethoxysilanes **1** to α,β -unsaturated carbonyl compounds **4** were shown in Scheme 2 and Table 3. Under the similar reaction condition to that used for the above 1,2-addition to **2**, the reaction of **4**, such as α,β -unsaturated ester **4a-c**, amide **4d**, and ketone **4e**, with **1** gave the desired the corresponding adducts **5** in 64–84% yields (entries 1 and 3-7). The addition of sodium hydroxide in such a case was also effective (entry 2), although the conjugated additions of arylsilanes without a basic activator have been reported.^{9,10}

<<Scheme 2>>

<<Table3>>

In conclusion, in the presence of aqueous sodium hydroxide, aryltriethoxysilane **1** was one of the most accessible alternative arylating reagents for the rhodium-catalyzed addition to carbonyl compounds **2** and **4**. Investigations for mechanistic studies and

additions to other carbonyl compounds are currently in progress in our laboratory.

Experimental Section

Representative Procedure for Addition of Aryltriethoxysilanes.

[Rh(OH)(cod)]₂ (0.0038 mmol) was placed in a test tube with septum rubber. The test tube was flushed with argon and then charged with 1,4-dioxane (1 ml), 1,5-cyclooctadiene (0.075 mmol), and 2.5 M NaOH aq. (0.1 ml, 0.25 mmol). Aryltriethoxysilane **1** (0.5 mmol) and carbonyl compounds **2** or **4** (0.25 mmol) were added successively. After being stirred at 90 °C for 16 h, the reaction mixture was diluted with ether and passed through a column of Na₂SO₄ (5 g) to dryness. The solvent was evaporated and product **3** or **5** was isolated by bulb-to-bulb distillation.

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[Single Column Table]

Table 1. Reaction of Phenyltriethoxysilane **1a** with Benzaldehyde **2a** under Various Conditions^a

entry	catalyst	base	solvent	yield (%) ^b
1	[RhOH(cod)] ₂	NaOH	dioxane	79
2 ^c	[RhOH(cod)] ₂	NaOH	dioxane	16
3	[RhCl(cod)] ₂	NaOH	dioxane	72
4	[Rh(cod) ₂]BF ₄	NaOH	dioxane	78
5	[RhOH(cod)] ₂	none ^d	dioxane	4
6	[RhOH(cod)] ₂	KOH	dioxane	57
7	[RhOH(cod)] ₂	KF	dioxane	19
8	[RhOH(cod)] ₂	CsF	dioxane	25
9	[RhOH(cod)] ₂	NaOH	DMF	10
10	[RhOH(cod)] ₂	NaOH	DME	48
11	[RhOH(cod)] ₂	NaOH	diglyme	51
12	[RhOH(cod)] ₂	NaOH	toluene	34

^a Reactions of **1a** (0.50 mmol) with **2a** (0.25 mmol) were carried out at 90 °C for 16 h in 1 ml of solvent by using a catalyst (3 mol% of rhodium metal), 1,5-cyclooctadiene (0.075 mmol), and an aqueous base (2.5M, 0.25 mmol). ^b GLC yields of **3a** are based on **2a**. ^c The reaction was carried out in the absence of 1,5-cyclooctadiene. ^d Water (0.1 ml) was used in place of the aqueous base.

Table 2. Addition of **1** to **2**

entry	arylsilane 1	aldehyde 2	yield (%) ^a
1	PhSi(OMe) ₃	2a	(55)
2	PhSi(OMe) ₂ Me	2a	(13)
3	PhSiCl ₂ Me	2a	(0)
4	PhSiMe ₃	2a	(13)
5	1b	2a	71
6	1c	2a	83
7	1a	2b	74
8 ^b	1a	2c	70
9 ^c	1a	2d	50

^a Isolated yields are based on **2**. ^b 1,5-Cyclooctadiene (0.6 equiv) was used. ^c The reaction was carried out at 120 °C in the presence of 1.0 equiv of 1,5-cyclooctadiene.

Table 3. Conjugated Addition of **1** to **2**^a

entry	arylsilane 1	carbonyl compounds 4	yield (%) ^b
1	1a	4a	(78)
2 ^c	1a	4a	(53)
3	1d	4a	83
4	1a	4b	84
5	1a	4c	88
6	1a	4d	64
7	1a	4e	81

^a Reactions of **1** (0.50 mmol) with **4** (0.25 mmol) were carried out at 90 °C for 16 h in THF (1 ml) by using [Rh(OH)(cod)]₂ (3 mol% of rhodium metal), 1,5-cyclooctadiene (0.075 mmol), and NaOH (2.5M aqueous solution, 0.25 mmol). ^b Isolated yields are based on **4**. Yields in parentheses are GLC yields. ^c Water (0.1 ml) was used in place of the aqueous NaOH.

[Graphic Abstract]

