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Rh-catalyzed 1,4-addition of triallyl(aryl)silanes to α,β-unsaturated carbonyl compounds

Toshiyuki Kamei *, Mizuho Uryu, Toyoshi Shimada *

Department of Chemical Engineering, Nara National College of Technology, 22 Yata-cho, Yamatokoriyama, Nara 639-1080, Japan

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Rh-catalyzed 1,4-addition of triallyl(aryl)silane to α,β-unsaturated carbonyl compounds was developed. Triallyl(aryl)silanes were used as air- and moisture-stable silicon nucleophiles. Allylsilanes were converted to silanols in situ and underwent transmetalation. This method can accept a wide range of functionalized triallyl(aryl)silane and α,β-unsaturated carbonyl compounds.

Rh-catalyzed 1,4-addition to α,β-unsaturated carbonyl compounds is one of the most useful C–C bond-forming reactions in organic synthesis.[1] Since the pioneering work by Miyaura and co-workers, Rh-catalyzed 1,4-addition of organoborane reagents has been well-studied because of their reactivity, selectivity, stability, and commercial availability.[2]

Organosilicon reagents are also attractive in the view of their stability, lack of toxicity, and large abundance. However, applicable organosilicon reagents have been limited to organo(trialkoxy)silanes,[3] organosilanediols,[4] and halosilanes,[5] which are unstable under hydrolytic conditions.[6] In contrast, tetraorganosilane reagents are easily handled under air and moisture conditions, but are less reactive in silicon to rhodium transmetalation. To overcome this limitation, Nakao, Hiyama, Hayashi and co-workers developed 1,4-addition with organo[(2-hydroxymethyl)phenyl]dimethylsilanes, which were stable but reactive tetraorganosilane reagents that could be controlled by placing a protective group on the hydroxy functionality.[7] This methodology was the powerful tool to develop 1,4-addition using organosilicon reagents, except for the preparation of starting materials.

In our laboratory, allylsilanes were found to act as silanol precursors for functionalization of the silica surface and preparation of organic–inorganic hybrid materials.[8] Allylsilanes can tolerate the further functionalization and purification using silica-gel column chromatography, but can be hydrolyzed under acidic condition generating propene. Moreover aryl(allyl)silanes were easily prepared from corresponding aryllithium or aryl magnesium reagent with halosilanes.[9] Previously, Nakao and Hiyama reported the efficient Si to Pd transmetalation in cross-coupling reaction using triallyl(aryl)silanes as silicon nucleophiles.[10] We envisioned that triallyl(aryl)silane was applied to Rh-catalyzed 1,4-addition to α,β-unsaturated carbonyl compounds.

We initially investigated the reaction of cyclohexen-2-one (**2a**) with triallyl(phenyl)silane (**1a**) catalyzed by $[Rh(cod)(CH_3CN)_2]BF_4$/(*S*)-BINAP which have been developed by Oi and Inoue[3a] using trialkoxy(aryl)silanes as silicon reagents. However, conversion of allylsilane to silanol was unsuccessful (Table 1, entry 1) to recover the starting materials. This result showed that the reactivity of triallyl(phenyl)silane was low and hydrolysis of allylsilane should be needed to give transmetalation-active silanol intermediate.

The additives were evaluated to determine if they improved the hydrolysis of allylsilane. Addition of KOH as a strong base resulted in no reaction and complete recovery of **1a** (entry 2). Activation of **1a** with fluoride ion source, $TBAF{\cdot}3H_2O$ (entry 3), succeeded in giving 3-phenylcyclohexanone (**3aa**) in 33% yield. $[RhCl(cod)]_2$ slightly enhanced the reactivity to afford the product in 44% yield (entry 4). Reaction without addition of BINAP also succeeded (entries 6–9). In the absence of Rh catalyst, the mixture of silanol and siloxane were detected, but 1,4-addition did not succeed to recover **2a** (entry 5). Reaction at a lower temperature improved the yield, due to suppression of the protodesilylation of aryl group (entry 7). Addition of half equivalent of $TBAF{\cdot}3H_2O$ gave the best result to afford **3aa** in 83% yield (entry 8). The less amount of

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* Corresponding authors. Tel.: +81 743 55 6155; fax: +81 743 55 6169.
E-mail addresses: kamei@chem.nara-k.ac.jp (T. Kamei), shimada@chem.nara-k.ac.jp (T. Shimada).

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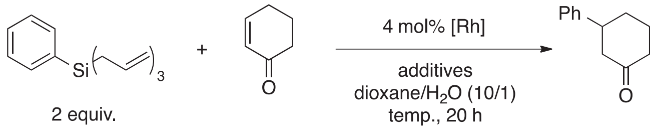
0040-4039/

Table 1
Screening of reaction conditions for Rh-catalyzed 1,4-addition of triallyl(phenyl)silane



2 equiv.
1a **2a** **3aa**

Entry	Rh catalyst	Temp (°C)	Additives (equiv)	Yield[a]
1	$[Rh(cod)(MeCN)_2]BF_4$ (*S*)-BINAP	90	None	N.R.
2	$[Rh(cod)(MeCN)_2]BF_4$ (*S*)-BINAP	90	KOH (1.0)	N.R.
3	$[Rh(cod)(MeCN)_2]BF_4$ (*S*)-BINAP	90	TBAF·$3H_2O$ (1.0)	33
4	$[RhCl(cod)]_2$[c] (*S*)-BINAP	90	TBAF·$3H_2O$ (1.0)	44
5	None	90	TBAF·$3H_2O$ (1.0)	0[d]
6	$[RhCl(cod)]_2$[c]	90	TBAF·$3H_2O$ (1.0)	10
7	$[RhCl(cod)]_2$[c]	50	TBAF·$3H_2O$ (1.0)	50
8	$[RhCl(cod)]_2$[c]	50	TBAF·$3H_2O$ (0.5)	83 (73)[b]
9	$[RhCl(cod)]_2$[c]	50	TBAF·$3H_2O$ (0.1)	38
10	$[Rh(OH)(cod)]_2$[c]	50	TBAF·$3H_2O$ (0.5)	89 (80)[b]
11	$[Rh(cod)(MeCN)_2]BF_4$	50	TBAF·$3H_2O$ (0.5)	7
12	$[Rh(cod)_2]BF_4$	50	TBAF·$3H_2O$ (0.5)	12

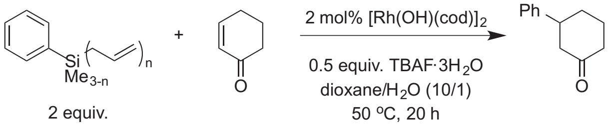
[a] GC yield.
[b] Isolated yield in the parentheses.
[c] 2 mol %.
[d] Arylsilanol and arylsiloxane were observed.

TBAF·$3H_2O$ diminished conversion of **1a** to give **3aa** in lower yields (entry 9). Although $[Rh(OH)(cod)]_2$ was also good catalyst for this reaction (entry 10), cationic rhodium complexes were not efficient catalysts (entry 11 and 12).

Next, we investigated on the effect of the number of allyl groups on yields (Table 2), using addition to cyclohexenone (**1a**) catalyzed by $[Rh(OH)(cod)]_2$ as a model reaction. Diallyl(methyl)phenylsilane (**4**) decreased the yield of **3aa** (entry 2), although aryldimethylsilanols can act as reactive silicon nucleophiles in Pd-catalyzed cross-coupling reaction,[11] diallyl(methyl)phenylsilane. Subjecting allyl(dimethyl)phenylsilane (**5**) to the condition resulted in recovery of starting materials.[10a] These results indicated that the number of allyl groups were important for the transmetalation from silicon to rhodium and for the hydrolysis of allyl groups.

Next, we examined the substrate scope of the reaction (Table 3). Cyclopentenone (**2b**) was a good substrate for this reaction to convert to 3-phenylcyclepentanone (**3ab**). Reaction with hept-3-en-2-one (**2c**) also proceeded, albeit in lower yields (entry 3). 1-Phenyl-2-hexen-1-one (**2d**) was also available for the 1,4-addition (entry 4). Although the addition to the ester **2e** successfully gave **3ae** in 82% yield (entry 5), addition to amide **2f** failed to furnish the desired product (entry 6).

Table 2
Effect of the number of allylsilane on yield



2 equiv.
2a **3aa**

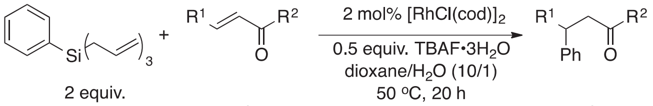
Entry	*n*	Yield[a]
1	3 (**1a**)	80
2	2 (**4**)	35
3	1 (**5**)	Trace

[a] GC yield.

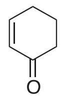
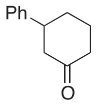
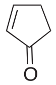
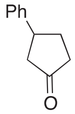
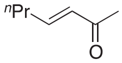
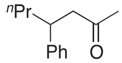
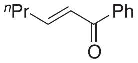
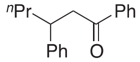
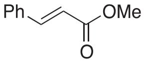
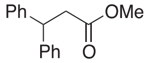
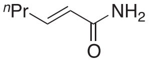
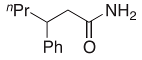
For further investigation of the substrate scope, the reaction was conducted with a variety of triallyl(aryl)silanes (Table 4). Arylsilanes with electron-donating groups, such as methyl (**1b–d**, entries 1–5) or methoxy (**1e–g**, entry 6–8), underwent the reaction, leading to products in moderate to high yields. Arylsilane with an electron-withdrawing fluoro and trifluoromethyl group (**1h–i**, entries 9–13) was also reactive toward Rh-catalyzed 1,4-addition.

In conclusion, a strategy for Rh-catalyzed 1,4-addition using triallyl(aryl)silanes was developed. Allylsilanes were hydrolyzed in situ to form transmetalation-active arylsilanol intermediates. Three allyl groups on silicon were required for successful reaction, promoting transmetalation and hydrolysis of the allyl groups.

Table 3
Rh-catalyzed 1,4-addition to various carbonyl compounds

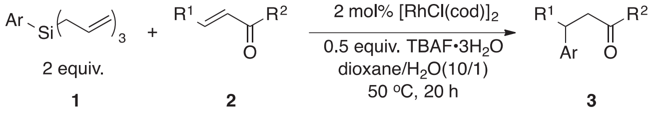


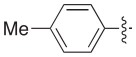
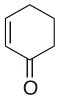
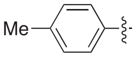
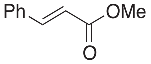
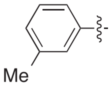
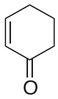
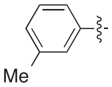
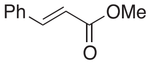
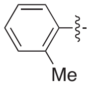
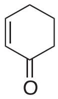
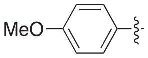
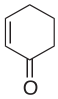
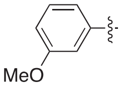
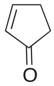
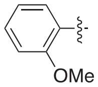
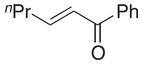
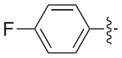
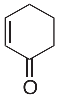
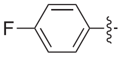
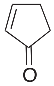
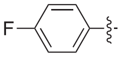
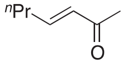
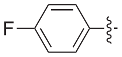
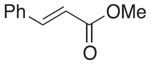
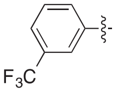
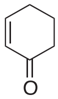
2 equiv.
1a **2** **3**

Entry	2		3		Yield
1[a]		**2a**		**3aa**	80
2		**2b**		**3ab**	93
3		**2c**		**3ac**	38
4		**2d**		**3ad**	75
5		**2e**		**3ae**	82
6		**2f**		**3af**	Trace

[a] $[Rh(OH)(cod)]_2$ was used instead of $[RhCl(cod)]_2$.

Table 4
Rh-catalyzed 1,4-addition of various triallyl(aryl)silane to α,β-unsaturated carbonyl compounds



Entry	1		2		3	Yield
1[a,e]		**1b**		**2a**	**3ba**	45
2[d]		**1b**		**2e**	**3be**	84
3		**1c**		**2a**	**3ca**	55
4[c,d]		**1c**		**2e**	**3ce**	49
5		**1d**		**2a**	**3da**	67
6[a,b,d]		**1e**		**2a**	**3ea**	67
7[a]		**1f**		**2b**	**3fb**	76
8[d]		**1g**		**2d**	**3hd**	67
9		**1h**		**2a**	**3ia**	46
10[d]		**1h**		**2b**	**3ib**	60
11[d]		**1h**		**2c**	**3ic**	20
12[d]		**1h**		**2e**	**3ie**	34
13		**1i**		**2a**	**3ja**	64

[a] $[Rh(OH)(cod)]_2$ was used instead of $[RhCl(cod)]_2$.
[b] TBAF (0.1 equiv).
[c] TBAF (1 equiv).
[d] At 70 °C.
[e] At 90 °C.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.03.002.

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