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Silicone as an Organosilicon Reagent 2. Rhodium-Catalyzed Conjugate Addition of the Silicone Reagent to α,β-Unsaturated Carbonyl Compounds

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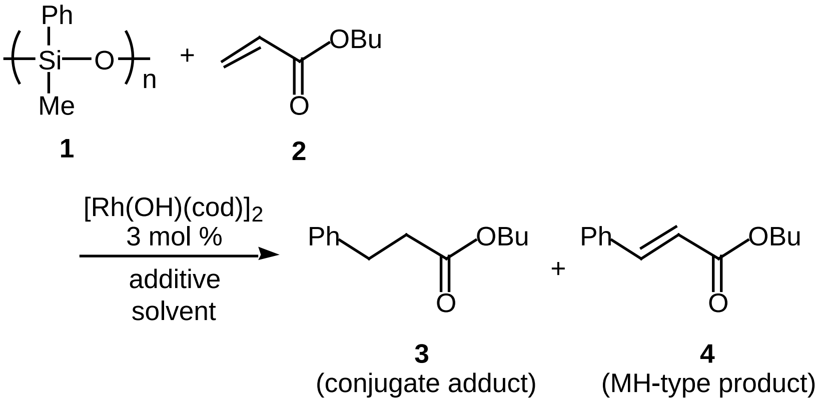
Abstract: The reaction of poly(phenylmethylsiloxane) with α,β–unsaturated carbonyl compounds in the presence of aqueous K_2CO_3 and 3 mol % of $[Rh(OH)(cod)]_2$ gives 1,4-conjugate addition product in good yields. Arylchlorosilanes also undergo the conjugate addition in excellent yields under similar conditions.

Key words: silicone, rhodium complex, conjugate addition, potassium carbonate, arylchlorosilanes

We have recently reported that silicone, poly(diorganosiloxane), is available as a new class of organosilicon reagent for palladium-catalyzed cross-coupling reaction with organic halides using silver(I) oxide or tetrabutylammonium fluoride (TBAF) as an activator.[1] Poly(phenylmethylsiloxane) (**1**), which is industrially utilized as highly thermo-resistant silicone oil, serves as an organic nucleophilic reagent for the coupling reaction.[2] The results showed that siloxane is also available for the reactions that proceed with silanols, silanediols, and silanetriols.[3] Our interest thus turned to develop another class of transition metal-catalyzed carbon-carbon bond-forming reactions. In this paper we report that rhodium-catalyzed conjugate addition of *silicone* to α,β-unsaturated carbonyl compounds also takes place efficiently when an aqueous base is employed to activate the silicone reagent.[4–5] In addition, the reaction with chlorosilanes in the presence of K_2CO_3, with which oligosiloxanes are formed in situ, is described.

In the rhodium-catalyzed reactions of silanediols with α,β-unsaturated esters, the reaction course (conjugate addition vs Mizoroki-Heck (MH)-type reaction) was controllable on the basis of reaction conditions.[4,6] The reaction of the silicone reagent **1**[2] with butyl acrylate (**2**) was thus carried out similarly (eq 1). As shown in Table 1, neither the MH-type reaction (entry 1) nor the conjugate addition (entry 2) was found to occur under the similar conditions to the reaction with silanediol.[4] However, addition of an aqueous base to the reaction of **1** with **2** in 1,4-dioxane at an elevated reaction temperature affected the conjugate addition to give **3** in a moderate yield. Among several bases employed, potassium carbonate was found to be effective (entries 3-5). On the other hand, the MH-type reaction that had been carried out with silanediols under non-aqueous conditions was achieved in aqueous toluene to afford **4** in 35% yield along with 7% of **3** (entry 6).



equation 1.

insert Table 1 here

It is remarkable that the conjugate addition of polysiloxane **1** to α,β-unsaturated carbonyl compounds bearing a substituent at the β-position **5a-e** occurs in toluene-H_2O at 120 ˚C in the presence of K_2CO_3 as shown in Table 2.[7] The reaction of ethyl cinnamate (**5a**) afforded the corresponding conjugate addition product **6a** in 78% yield. Several unsaturated ketones and esters with various substituents similarly underwent the reaction.

insert Table 2 here

Treatment of polysiloxane with aqueous potassium carbonate would partially cleave siloxane to form oligosiloxane segments that facilitate migration of the aryl group. Thereby, we envisaged that the similar conjugate addition with chlorosilanes could also be possible since treatment of the chlorosilane with aqueous alkaline solution furnished oligosiloxane.[3a,8] Indeed, the mixture of phenyltrichlorosilane (**7**) and potassium carbonate was subjected to the reaction of (*E*)-4-phenyl-3-butene-2-one (**5d**) to afford 72% of the conjugate addition product **6d** after stirring in toluene-H_2O (8:1) at 120 ˚C for 24 h. Table 3 shows the reaction of various arylchlorosilanes with α,β-unsaturated carbonyl compounds. When **7** was employed as a substrate, use of three equivalents of K_2CO_3 toward the chlorosilane was found to be the best. On the other hand, use of 1.5 equiv of K_2CO_3 resulted in no reaction and excess amounts of K_2CO_3 also decreased the yield of **6**. The trichlorosilane **7** was similarly subjected to the reaction of several α,β-unsaturated carbonyl compounds to afford the conjugate addition products in good yields. In addition, several aryldichlorosilanes **8**-**10** and phenyldimethylchlorosilane (**11**) were also found to affect the conjugate addition.

insert Table 3 here

In summary, we have shown that silicone and chlorosilanes undergo conjugate addition to α,β-unsaturated carbonyl compounds with rhodium catalyst. Although the reactions require highly active rhodium catalyst and a higher reaction temperature compared to those with organoboron reagents, it is remarkable that silicone and chlorosilanes that are industrially available organosilicon compounds affect carbon-carbon bond-forming reactions by the catalysis of rhodium complexes. Further investigation for several organic transformation reactions with such compounds as an organosilicon reagent is in progress by using transition metal complexes as catalysts.

Typical experimental procedure for the conjugate addition of 1 to α,β–unsaturated carbonyl compounds: To a solution of poly(methylphenylsiloxane) (**1**, 81.9 mg, 0.6 mmol) in 2 mL of toluene was added an aqueous solution of potassium carbonate (27.6 mg, 0.2 mmol in 0.2 mL of water). The resulting mixture was stirred at room temperature for 1 h. After stirring the mixture, (*E*)-4-phenyl-3-buten-2-one (**5d**, 29.2 mg, 0.2 mmol) and $[Rh(OH)(cod)]_2$ (2.8 mg, 0.006 mmol) were added, and the resulting yellow solution was stirred at 120 ˚C for 24 h. After cooling to room temperature, the organic layer was separated and aqueous was extracted with diethyl ether (10 mL x 2). The combined organic layers were washed with 1 M HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL), and dried over anhydrous magnesium sulfate. Removal of the solvent left a crude oil, which was subjected to chromatography on silica gel (reverse phase, methanol/H_2O = 9/1) to afford 53.8 mg of 4,4-diphenyl-butan-2-one (**6d**, 80%).[9]

Typical experimental procedure for conjugate addition of organochlorosilanes to α,β–unsaturated carbonyl compounds (representative as the reaction of 8 and 5a): To a solution of potassium carbonate (10.37 g, 75 mmol) in 40 mL of toluene and 10 mL of water was added phenylmethyldichlorosilane (**8**) (4.77 g, 25 mmol). After stirring the mixture at room temperature for 2 h, (*E*)-ethyl 3-phenylpropenoate (**5a**) (0.88 g, 5 mmol, $[Rh(OH)(cod)]_2$ (70 mg, 0.15 mmol) and 10 mL of toluene were added. The resulting mixture was stirred at 120 ˚C for 41 h. After cooling the mixture to room temperature, the organic layer was separated and aqueous was extracted with diethyl ether (20 mL x 2). The combined organic layer was washed with 1 M HCl (30 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL). Removal of the dried solvent with anhydrous magnesium sulfate and chromatography on silica gel (hexane/AcOEt = 10:1) afforded 1.23 g of ethyl 3,3-diphenylpropanoate (**6a**, 97%).[9]

Acknowledgment

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(1) Mori, A.; Suguro, M. *Synlett* **2001**, 845.

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(7) Although we described that the reaction of silanediol with β-substituted substrates did not occur (ref 4) under the reported conditions, further optimization revealed to undergo the conjugate addition of such substrates with silanediol recently. These results will be described in due course.

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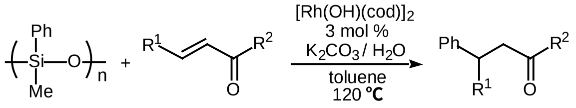
(9) All products were identical with authentic samples.

Table 1 Conjugate addition of **1** to **2**[a]

entry	solvent	additive	%yield of **3**	 **4**
1[b]	THF	none	0	0
2[b]	THF-H_2O	none	0	0
3	1,4-dioxane-H_2O	K_2CO_3	46	8
4	1,4-dioxane-H_2O	NaOH	33	0
5	1,4-dioxane-H_2O	KOH	29	0
6	toluene-H_2O	K_2CO_3	7	35

[a] Unless otherwise noted, the reaction was carried out with **2** (0.2 mmol), **1** (0.6 mmol) and 3 mol % of $[Rh(OH)(cod)]_2$ at 100 ˚C and the yields were estimated by ^{1}H NMR. [b] The reaction was carried out at 70 ˚C.

Table 2 Conjugate addition of **1** to **5**

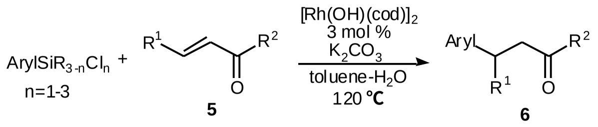


1 **5** **6**

entry	α,β-unsaturated carbonyl compound **5**	%yield of **6**
1	(*E*)-PhCH=CHCOOEt (**5a**)	78
2	(*E*)-EtOCOCH=CHCOOEt (**5b**)	49
3	(*E*)-CH_3CH=CHCOOMe (**5c**)	51
4	(*E*)-PhCH=$CHCOCH_3$ (**5d**)	80
5	(*E*)-PhCH=CHCOPh (**5e**)	>99

The reaction was carried out with **1** (0.6 mmol), **5** (0.2 mmol), K_2CO_3 (0.2 mmol), and 3 mol % of the rhodium catalyst in toluene-H_2O (2 mL/0.2 mL) at 120 ˚C for 24 h.

Table 3 Conjugate addition of chlorosilanes to **5**[a]



entry	ArylSiR$_{3-n}$Cl$_n$ (n=1-3)		chlorosilane/ K$_2$CO$_3$	**5**		%yield of **6**
1	PhSiCl$_3$	(**7**)	3.0	(*E*)-PhCH=CHCOOEt	(**5a**)	80
2	**7**		3.0	(*E*)-PhCH=CHCOCH$_3$	(**5d**)	72
3	**7**		4.5	**5d**		44
4	**7**		1.5	**5d**		0
5	**7**		3.0	(*Z*)-MeOCOCH=CHCOOMe	(**5f**)	78
6	**7**		3.0	(*E*)-^{n}C$_5$H$_{11}$CH=CHCOCH$_3$	(**5g**)	77
7	PhSiMeCl$_2$	(**8**)	2.0	2-cyclohexen-1-one	(**5h**)	70
8	**8**		2.0	**5a**		91
9	4-MeOC$_6$H$_4$SiEtCl$_2$	(**9**)	2.0	**5a**		>99
10	4-CF$_3$C$_6$H$_4$SiEtCl$_2$	(**10**)	2.0	**5a**		73
11	PhSiMe$_2$Cl	(**11**)	1.0	**5a**		>99

[a] Unless otherwise noted, the reaction was carried out with **5** (0.3 mmol), chlorosilane (0.6-1.5 mmol) and 3 mol % of [Rh(OH)(cod)]$_2$ in toluene-H$_2$O at 120 ˚C for 24 h.

Graphical abstract

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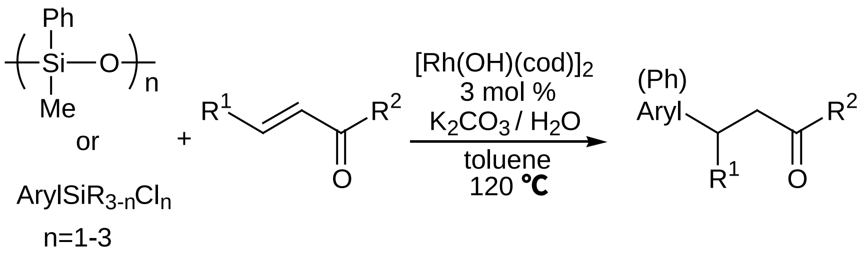

silicone, rhodium compex, conjugate addition,
potassium carbonate, arylchlorosilanes