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Rhodium-catalyzed substitution of allylic carbonates with enoxysilanes

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Abstract

Substitution at the allylic position proceeds smoothly in rhodium-catalyzed reactions of allyl carbonates with enoxysilanes under almost neutral conditions to give γ,δ-unsaturated ketones in good to excellent yields. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: rhodium; cation complex; catalyst; enoxysilane; allylation.

Transition-metal catalysts have been explored as a powerful tool for carbon–carbon bond formation under mild conditions. Although there have been many reports on the substitution of allylic derivatives catalyzed by palladium,[1] nickel,[2] molybdenum,[3] iron,[4] tungsten,[3a,5] or ruthenium[6] complexes, only a few examples of the rhodium-catalyzed allylic substitution have been reported.[2k,7] Moreover, there are exceptional reports showing the successful use of enoxysilanes in place of soft carbanions as a nucleophile under neutral conditions in an allylic substitution.[3a,4b,8]

We have already reported rhodium-catalyzed Mukaiyama-type aldol coupling of enoxysilanes (**1**) with aldehydes or ketones under neutral conditions,[9] in which it is pointed out that the rhodium enolate complex, **2**, plays an important role (Scheme 1). If this is the case, allyl carbonate (**4**) would behave as an electrophile in the coupling with an enoxysilane (**1**). Thus, we designed rhodium-catalyzed reactions of **1** with **4**. Here we report successful substitution of allylic carbonates with enoxysilanes in the presence of a cationic rhodium catalyst to give the γ,δ-unsaturated ketones.

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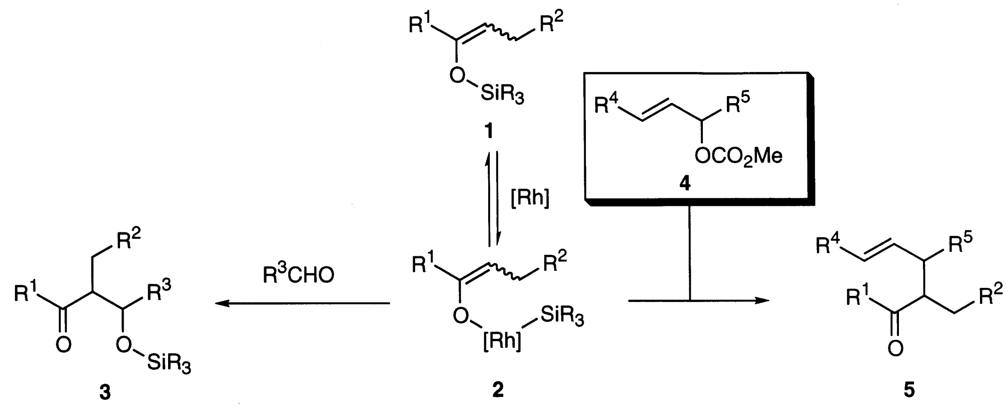
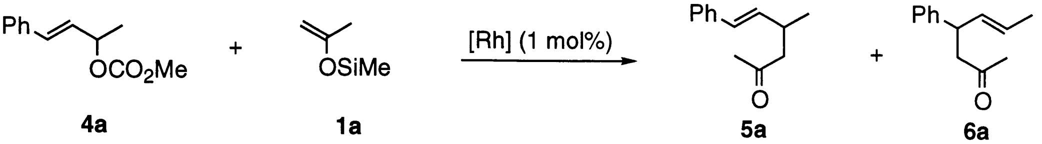


Scheme 1.

Firstly, when a mixture of allylcarbonate **4a** and 4 equivalents of **1a** in CH_2Cl_2 was heated at 80°C for 19 h in the presence of 1 mol% [Rh(COD)(DPPB)]OTf [**7a**, COD = 1,5-cyclooctadiene, DPPB = 1,4-bis(diphenylphosphino)butane] two products, **5a** and **6a** (**5a**:**6a** = 53:47) appeared, which were obtained as an unseparable mixture in 58% yield (67% conversion based on **4a**, entry 1 in Table 1). After several trials, the yield of products was remarkably improved by using 1

Table 1
Substitution of **4a** with **1a** catalyzed by rhodium complex[a]



Entry	Catalyst	Solvent	Conversion of **4a** (%)	Product[10]	
				Yield (%)[b]	Ratio (**5a**:**6a**)[c]
1	[Rh(COD)(DPPB)]OTf (**7a**)	CH_2Cl_2	67	58	53:47
2	[Rh(COD)($MePh_2P)_2$]OTf (**7b**)	CH_2Cl_2	100	86	52:48
3	$Rh_4(CO)_{12}$ (**7c**)	CH_2Cl_2	48	42	55:45
4	[Rh(COD)($Me_2PhP)_2$]OTf (**7d**)	CH_2Cl_2	100	76	55:45
5	**7b**	CH_3CN	100	100	55:45
6	**7b**	THF	100	66	51:49
7	**7b**	C_6H_6	100	63	58:42
8	**7b**	DMSO	–[d]	0	–

[a] A mixture of **4a** (0.7–1 mmol), **1a** (4 equiv. for **4**), and **7** (1 mol% for **4**) in the solvent was heated in a sealed tube for 19 h at 80°C.

[b] Isolated yield.

[c] Determined by GLC analyses.

[d] Not determined.

mol% of $[Rh(COD)(MePh_2P)_2]OTf$ (**7b**) as a catalyst under similar reaction conditions, although the regioselectivity was not altered (86% isolated yield, entry 2 in Table 1). Other rhodium complexes, such as $Rh_4(CO)_{12}$ (**7c**, entry 3 in Table 1) and $[Rh(COD)(Me_2PhP)_2]OTf$ (**7d**, entry 4 in Table 1) were less effective than **7b**, and $RhCl(PPh_3)_3$, $Rh(CO)_2(acac)$, $Rh(C_2H_4)_2(acac)$, $RhH(PPh_3)_4$, $[Rh(COD)(DPPB)]PF_6$, $[Rh(COD)(DPPB)]BF_4$, $[Rh(COD)(PPh_3)_2]PF_6$ exhibited no catalytic activity for the coupling under similar conditions. The efficacy of **7b** was also affected by the solvent in the reaction of **1a** with **4a**. The reaction in CH_3CN (100% isolated yield, entry 5 in Table 1) progressed smoothly at a similar level to that in CH_2Cl_2. The catalysts worked in THF (66% isolated yield, entry 6 in Table 1) and in benzene (63% isolated yield, entry 7 in Table 1) albeit with less efficiency than that in CH_2Cl_2, while the reaction did not proceed at all in DMSO.

Other types of allylic carbonates and enoxysilanes were subjected to the reaction for exploring the scope of the present rhodium-catalyzed substitution of **4**. The results are summarized in Table 2. Linear allylic carbonates were uniformly converted into the corresponding γ,δ-unsaturated ketones in high yield from the reactions with **1a** (entries 1–6 in Table 2). Almost identical results were obtained in the reaction of **1a** with either a cinnamyl derivative (**4d**) or its regioisomer (**4e**) to give the corresponding products **5d** and **6d** in 80% yield (entries 3 and 4 in Table 2). Disubstitution at the allylic terminus distal to the leaving group (**4g**) seems to improve the isomer ratio of the products (**5g**:**6g** = 3:1, entry 6 in Table 2). Cyclohexenyl derivatives (**4h** and **4i**) were also available to the coupling with **1a** under similar conditions to give **5h** and a mixture of **5i** and **6i** (**5i**:**6i** = 69:31), respectively, in moderate yield (entries 7 and 8 in Table 2). These results are in clear contrast to the fact that simple allylic carbonate (**4**, $R^4 = R^5 = H$) did not interact with **1a** under similar conditions.

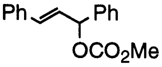
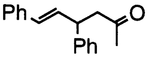
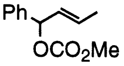
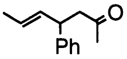
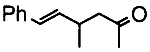
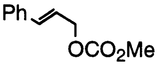
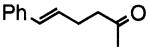
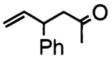
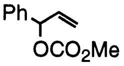
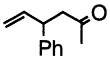
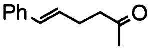
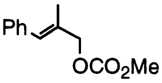
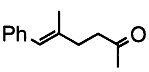
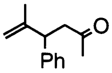
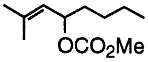
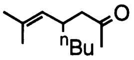
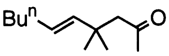
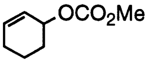
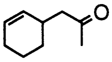
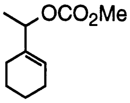
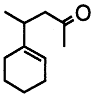
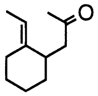
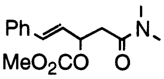
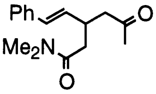
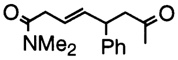
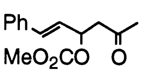
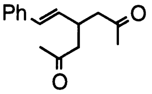
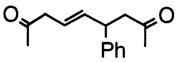
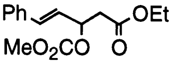
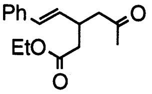
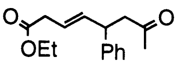
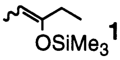
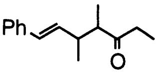
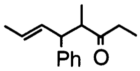
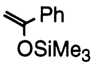
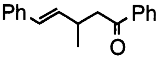
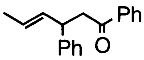
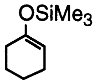
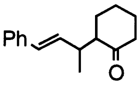
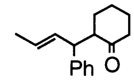
One of the most direct advantages to the operation under neutral conditions is that the designed transformation is applicable to substrates bearing functional groups susceptible to an acid or a base. In fact, the functional groups such as carbamoyl, carbonyl (ketone), and alkoxy carbonyl groups remained intact during the reactions of **4j**, **4k**, and **4l** with **1a** to give the corresponding products in high to moderate yields (entries 9–11 in Table 2).

High yields of products were also observed in the reactions of linear enoxysilane **1b** and **1c** with **4a** (entries 12 and 13 in Table 2). In contrast to these results, a coupling reaction of **4a** with 1-trimethylsilyloxycyclohexene **1d** gave the corresponding products only in 30% yield (**8ad**:**9ad** = 54:46, entry 14 in Table 2). The low reactivity of cyclic enoxysilane (**1d**) might be attributed to the steric hindrance and/or *E* configuration of the olefinic part.

Although a pathway to the products is also elucidated by the intermediacy of the η^3-allyl rhodium complex in addition to our working hypothesis, as shown in Scheme 1, any information with respect to the mechanistic consideration is not obtained at present.

In summary, we have shown that enoxysilanes are endowed with sufficient nucleophilicity in the substitution of **4** catalyzed by cationic rhodium complexes under neutral conditions. The present operation provides a facile method for the chemoselective homologation of allylic carbonates involving other functions such as amide, ketones, and ester, which remain intact even in the reaction without a procedure for protection.

Table 2
Substitution of **4** with **1** catalyzed by **7b**[a]

entry	allylic carbonate 4		enoxysilane 1	product[10]					
						ratio[b]			yield (%)[c]
1		**4b**	**1a**		**5b**				76
2		**4c**	**1a**		**6a**	(44:56)		**5a**	92
3		**4d**	**1a**		**5d**	(68:32)		**6d**	79
4		**4e**	**1a**		**6d**	(36:64)		**5d**	80
5		**4f**	**1a**		**5f**	(68:32)		**6f**	86
6		**4g**	**1a**		**5g**	(74:26)		**6g**	72
7		**4h**	**1a**		**5h**				55
8		**4i**	**1a**		**5i**	(69:31)		**6i**	26
9		**4j**	**1a**		**5j**	(43:57)		**6j**	84
10		**4k**	**1a**		**5k**	(47:53)		**6k**	75
11		**4l**	**1a**		**5l**	(28:72)		**6l**	71
12		**4a**	 **1b**		**8ab**	(52:48)		**9ab**	91[d]
13		**4a**	 **1c**		**8ac**	(46:54)		**9ac**	90
14		**4a**	 **1d**		**8ad**	(54:46)		**9ad**	30

[a] A mixture of **4** (0.7-1 mmol), **1** (4 equiv. for **4**), and **7b** (1 mol% for **4**) in CH_2Cl_2 was heated in a sealed tube at 80 °C for 19 h. [b] Determined by GLC analyses. [c] Isolated yield. [d] The ratio of enoxysilane (*E* : *Z*) is 19 : 81.

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