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Rhodium-catalyzed carbonyl allylations by allylic alcohols with tin(II) chloride

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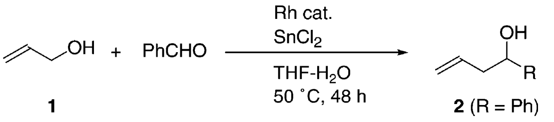
Abstract—Rhodium complexes such as $[RhCl(cod)]_2$, $[Rh(cod)_2]BF_4$, and $[Rh(cod)(CH_3CN)_2]BF_4$ function as catalysts for carbonyl allylations by allylic alcohols with 1 equimolar amount of tin(II) chloride to each allylic alcohol and aldehyde in THF at 50 °C to produce the corresponding homoallylic alcohols.

Palladium-catalyzed carbonyl allylation by allylic alcohols is a versatile allylating method in terms of (1) operation: allylic alcohols are stable to air, water, and light; and (2) synthetic efficiency: usual starting materials such as allylic halides, esters, and ethers in carbonyl allylations are prepared from allylic alcohols.[1] The palladium-catalyzed carbonyl allylation, which occurs via umpolung (transmetallation) of π-allylpalladium complexes,[1] needs over two equimolar amounts of reducing agents such as tin(II) chloride,[2] triethylborane,[3] and indium(I) iodide,[4] to allylic alcohols and/or carbonyl compounds. Only complexes of group X elements have been found to catalyze the carbonyl allylation via this kind of umpolung. π-Allylrhodiums, derived from rhodium(I) complexes with allylic halides, tosylates, and carbonates, have been applied to reactions with nucleophiles.[5] We here report on a catalytic cycle of rhodium(I) for carbonyl allylation by allylic alcohols with 1 equimolar amount of tin(II) chloride to the allylic alcohols, of which actual allylating agents are probably not allyltin compounds but allylrhodium complexes, in contrast to palladium-catalyzed carbonyl allylation by allylic alcohols with tin(II) chloride.[6]



(1)

Catalytic activity of rhodium complexes and stoichiometry of tin(II) chloride were investigated for the allylation of benzaldehyde (1 mmol) with 2-propenol (**1**, 1.5 mmol) in THF (3 mL) and H_2O (0.1 mL) in the presence of Rh cat. (0.02 mmol) at 50 °C for 48 h under a nitrogen atmosphere, which produced 1-phenyl-3-buten-1-ol (**2**, R = Ph) (Eq. 1, Table 1). No allylation occurs without either Rh catalysts or tin(II) chloride. $[RhCl(cod)]_2$ exhibited a higher catalytic activity than $[Rh(cod)_2]BF_4$, $[Rh(cod)(CH_3CN)_2]BF_4$, or $RhCl(PPh_3)_3$ (entries 1 and 3–5). The character of ligands such as PPh_3, (8 mol%, 84%), $P(C_6F_5)_3$ (8 mol%, 85%) and dppe (4 mol%, 84%) to the conditions of entry 7 does not affect the allylation to afford **2** (R = Ph). The allylation without H_2O was slow (entry 2).[7] THF (76%) is superior to other solvents such as acetonitrile (61%) and 1,3-dimethylimidazolidin-2-one (38%) under

Table 1. Rhodium-catalyzed allylation of benzaldehyde with **1**

Entry	Rh cat.	$SnCl_2$ (mmol)	**2** (R = Ph), Yield[a] (%)
1	$[RhCl(cod)]_2$	1.5	76 (95[b])
2[c]	$[RhCl(cod)]_2$	1.5	44
3	$[Rh(cod)_2]BF_4$	1.5	43
4	$[Rh(cod)(MeCN)_2]BF_4$	1.5	30
5	$RhCl(PPh_3)_3$	1.5	14
6[d]	$[RhCl(cod)]_2$	1.0	70
7[d]	$[RhCl(cod)]_2$	1.2	90

[a] Isolated yields.[9]
[b] After stirring for 72 h.
[c] The allylation was carried out without H_2O.
[d] The reaction was carried out with **1** (1 mmol) in THF (1 mL) for 11 h.

Keywords: Nucleophilic addition; Carbonyl allylation; π-Allylrhodium; Tin(II) chloride.

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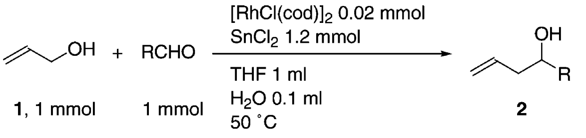
Table 2. Rhodium-catalyzed carbonyl allylation with **1**

Entry	R	Time (h)	**2**, Yield[a] (%)
1	$4\text{-ClC}_6\text{H}_4$	11	99
2	$4\text{-CH}_3\text{OOCC}_6\text{H}_4$	24	85
3	$4\text{-CH}_3\text{OC}_6\text{H}_4$	22	60
4	$(E)\text{-C}_6\text{H}_5\text{CH=CH}$	23	51
5	C_6H_{13}	17	88
6	$c\text{-C}_6\text{H}_{11}$	18	85

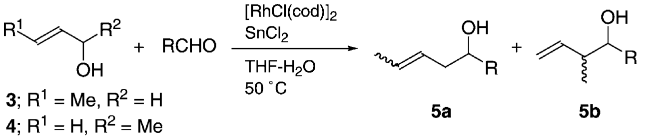
[a] Isolated yields.[9]

the conditions of entry 1. The allylation was quite slow at below 30 °C and might be followed by dehydration in refluxing THF.[8] The allylation was presumed to proceed with 1 equimolar amount of tin(II) chloride to each **1** and benzaldehyde, unlike palladium-catalyzed carbonyl allylations (entry 6).[2] The balance between the yield and the reaction rate determined optimal conditions; **1** (1.0 mmol), benzaldehyde (1.0 mmol), tin(II) chloride (1.2 mmol), and $[\text{RhCl(cod)}]_2$ (0.02 mmol) in THF (1 mL) and H_2O (0.1 mL) at 50 °C (entry 7). The allylation of various aldehydes with **1** was carried out under the optimal conditions (Eq. 2). Some representative results are summarized in Table 2. Aromatic aldehydes bearing an electron-withdrawing or electron-donating group, aliphatic aldehydes and α,β-unsaturated cinnamaldehyde can be employed in the rhodium-catalyzed allylation.



(2)

Regioselectivity and diastereoselectivity in the rhodium-catalyzed carbonyl allylation were investigated with (*E*)-2-buten-1-ol (**3**) and 3-buten-2-ol (**4**) (Eq. 3). The representative results are summarized in Table 3. Since the reactivity of **4** is higher than that of **3**, ease of π-coordination of C–C double bonds to rhodium may determine the reaction rates. The allylation of aromatic aldehydes with either **3** or **4** regioselectively occurred at the allylic position substituted by a methyl group to produce **5b** with slight *anti*-diastereoselectivity (entries 1–3 and 7–9). Regioselectivity in the allylation of aliphatic aldehydes was low (entries 5, 6, and 12).



(3)

NMR observation (JEOL Λ-500) of the reaction of 2-propen-1-ol (**1**, 1.0 mmol) with tin(II) chloride (1.2 mmol) in the presence of a catalytic amount of $[\text{RhCl(cod)}]_2$ (2 mol%) in THF-d_8 (0.75 mL) at 50 °C was carried out with neither any aldehydes nor any H_2O in a sealed tube. In distinction from palladium-catalyzed reaction,[2] the preparation of not 2-propenyltin intermediate but propene was confirmed: ^{1}H NMR (500 MHz) δ 1.68 (d, $J = 6.5$ Hz, 3H), 4.89 (d, $J = 10$ Hz, 1H), 4.98 (d, $J = 17$ Hz, 1H), 5.72–5.84 (m, 1H); ^{13}C NMR (125 MHz) δ 19.5, 115.9, 134.0. The preparation of propene without H_2O suggested that an allylhydridorhodium(III) complex could be prepared from an initial π- or σ-allylrhodium(III) complex such as **A** that should directly cause carbonyl allylation in the presence of aldehyde via the formation of σ-allylrhodium(III) complex **B** coordinated by the aldehyde (Scheme 1).[10] The comparison of regioselectivity between **3** and **4** suggested that initial 1-methyl-π-allylrhodium(III) complex could be transformed into σ-2-butenylrhodium(III) complex by a coordination of aldehyde and then the 2-butenyl moiety could cause γ-addition to the aldehyde. Since the reactivity of aliphatic aldehydes to the carbonyl allylation is low, γ-adducts **5b** produced initially may react with excess aldehydes to isomerize to α-adducts **5a** via the formation of homoallyloxycarbenium ion intermediates.[11]

In conclusion, we have established the Barbier-type rhodium(I)-catalyzed carbonyl allylation by allylic alcohols with tin(II) chloride. Noteworthy features are that (1) rhodium(I) complexes function as catalysts for carbonyl

Table 3. Rhodium-catalyzed carbonyl allylation with **3** and **4**

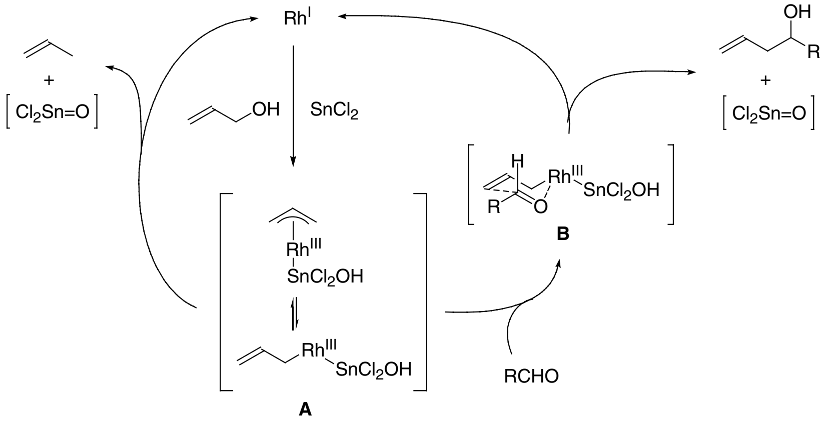
Entry	Allylic alcohol	R	Time (h)	Yield[a] (%)	**5a**/**5b** (*E*/*Z*, *syn*/*anti*)[b]
1[c]	**3**	C_6H_5	39	93	6/94 (75/25, 42/58)
2[c]	**3**	$4\text{-ClC}_6\text{H}_4$	39	97	9/91 (75/25, 34/66)
3[c]	**3**	$4\text{-CH}_3\text{OOCC}_6\text{H}_4$	39	99	10/90 (71/29, 32/68)
4[c,d]	**3**	$(E)\text{-C}_6\text{H}_5\text{CH=CH}$	29	39	0/~100 (—, 50/50)
5[c]	**3**	C_6H_{13}	35	78	33/67 (67/33, 62/38)
6[c]	**3**	$c\text{-C}_6\text{H}_{11}$	63	72	63/37 (77/23, 45/55)
7	**4**	C_6H_5	20	92	5/95 (65/35, 38/62)
8	**4**	$4\text{-ClC}_6\text{H}_4$	20	96	6/94 (65/35, 32/68)
9	**4**	$4\text{-CH}_3\text{OOCC}_6\text{H}_4$	16	93	8/92 (69/31, 29/71)
10	**4**	$(E)\text{-C}_6\text{H}_5\text{CH=CH}$	21	29	0/~100 (—, 50/50)
11	**4**	C_6H_{13}	19	95	6/94 (67/33, 70/30)
12	**4**	$c\text{-C}_6\text{H}_{11}$	21	81	27/73 (79/21, 33/67)

[a] Yields of mixtures of **5a** and **5b**.[9]

[b] The ratios were determined by 500 MHz ^{1}H NMR spectroscopy (JEOL Λ-500).

[c] The reaction was carried out with **3** (3.0 mmol) and $SnCl_2$ (3.0 mmol) in THF (2 mL).

[d] The reaction was carried out at 40 °C.



Scheme 1. A plausible catalytic cycle.

allylations by allylic alcohols, (2) a π- or σ-allylrhodium(III) stannate such as **A** seems to be an actual allylating agent though its direct detection by NMR observation has ended in failure, in distinction from palladium-catalyzed allylation,[2] (3) umpolung of π-allylrhodium complex has been appreciated first, and (4) the amount of tin(II) chloride used as a reducing agent can be cut down by using rhodium(I) complexes as catalysts instead of palladium complexes; 1 equimolar amount of tin(II) chloride to each allylic alcohol and aldehyde displays a sufficient effect.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.10.051.

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11. Nokami, J.; Ohga, M.; Nakamoto, H.; Matsubara, T.; Hussain, I.; Kataoka, K. *J. Am. Chem. Soc.* **2001**, *123*, 9168, The rhodium-catalyzed carbonyl allylation by **3** with excess benzaldehyde also led to low γ-regioselection; **3** (3 mmol), tin(II) chloride (2 mmol), benzaldehyde (5 mmol), THF (2 mL), H_2O (0.1 mL), 50 °C, 48 h, *y* 41%, $\alpha/\gamma = 34/66$.