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Rhodium-catalyzed allyl transfer from homoallyl alcohols to acrylate esters via retro-allylation

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Abstract—Retro-allylation of homoallyl alcohols by rhodium catalysts occurs to generate allylrhodium species. Insertion of acrylate esters to the allylrhodiums proceeds to give the corresponding 2,5-hexadienoate esters in situ. Subsequent isomerization or iterative 1,4-addition takes place in the same pots to furnish the corresponding 2,4-hexadienoate esters or triesters in good yields.

Metal-mediated retro-allylation of homoallyl alcohols is an interesting method for the generation of allylmetals, which proceeds through a carbon–carbon bond cleavage process. Our group[1] and others[2] reported allyl transfer from homoallyl alcohols to aldehydes, ketones, organic halides, and alkynes via retro-allylation. However, allyl transfer to alkenes has not been explored. Recently, we have found that the retro-allylation system could be applicable to rhodium catalysis and have achieved catalytic allyl transfer from homoallyl alcohols to aldehydes.[3] Herein, we wish to describe rhodium-catalyzed allyl transfer from homoallyl alcohols to activated alkenes, acrylate esters.

Treatment of diisopropyl-substituted homoallyl alcohol **1a′** (0.5 mmol) with butyl acrylate (**2a**, 2.0 mmol) in the presence of 2.5 mol % of $[RhCl(cod)]_2$, 10 mol % of $P(^cC_5H_9)_3$, and 15 mol % of cesium carbonate in refluxing toluene (5.0 mL) for 10 h provided butyl (*E*)-5-methyl-2,4-hexadienoate (**3aa**) in 18% yield (Table 1, entry 1). Apparently, methallyl transfer from **1a′** to **2a** occurred albeit the yield was low. The reaction would proceed via formation of σ-methallylrhodium, which would be in equilibrium with π-methallylrhodium, by retro-methallylation. With the interesting preliminary result, optimization studies were performed. Diphenyl substitution at the oxygenated carbon of homoallyl alcohol improved the yield to 29% (entry 2). Given that **1a** is the more acidic alcohol than **1a′**, the final protonolysis would be crucial to complete the catalytic cycle (vide infra). According to the assumption, we screened a variety of Brønsted acids as a mediator in the protonolysis step. Although benzoic acid suppressed the reaction completely (entry 3), phenol increased the yield to 37% (entry 4). The electron-withdrawing group on the aromatic ring gave no effect on yield (entry 5). Interestingly, sterically demanding 2-*tert*-butylphenol led to the formation of **3aa** in 48% yield (entry 6). Finally, with 5 mol % of $[RhCl(cod)]_2$, 20 mol % of $P(^cC_5H_9)_3$, 30 mol % of cesium carbonate, and 20 mol % of 2-*tert*-butylphenol, the desired product **3aa** was obtained in 70% yield (entry 7).

By using the optimized conditions, we conducted the allyl transfer from homoallyl alcohols **1a**–**d** bearing substituents at the β-position of the allyl moiety to acrylate esters **2** (Table 2). Although the reaction of **1a** with bulky ester **2b** gave a trace amount of the desired product (entry 2), the allyl transfer to acrylamide **2c** proceeded to produce 5,*N*,*N*-trimethyl-2,4-hexadienamide (**3ac**) in moderate yield (entry 3). The phenyl-substituted allyl moiety of homoallyl alcohol **1b** could also be transferred to **2a** to give the corresponding hexadienoate **3ba** in good yield with modest (*E*) selectivity (entry 4). Methyl acrylate (**2d**) as well as butyl acrylate (**2a**) participated in the reaction (entry 5). Electron-rich and electron-deficient substitutions on the benzene ring had moderate influence on yield and stereoselectivity (entries 6–9).

Keywords: Allyl transfer; Allylrhodium; Carbon–carbon bond cleavage; Retro-allylation.

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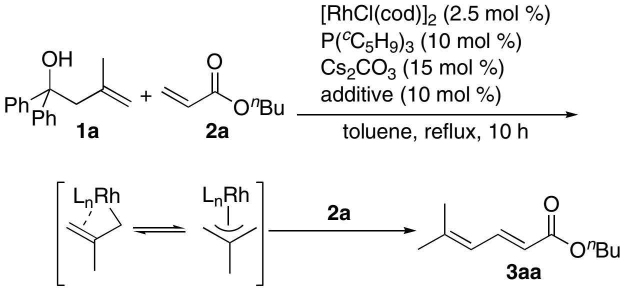
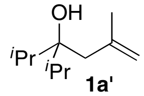
Table 1. Optimization for methallyl transfer from **1a** to **2a** via retro-methallylation



Entry	Additive	Yield of **3aa**[a] (%)
1[b]	None	18
2	None	29
3	Benzoic acid	0
4	Phenol	37
5	4-Trifluoromethylphenol	38
6	2-*tert*-Butylphenol	48
7[c]	2-*tert*-Butylphenol	70

[a] Determined by ^{1}H NMR.

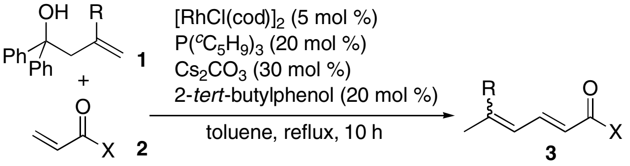
[b] Diisopropyl-substituted homoallyl alcohol **1a′** was used instead of **1a**.



1a'

[c] With 5 mol % of [RhCl(cod)]$_2$, 20 mol % of P(^{c}C$_5$H$_9$)$_3$, 30 mol % of cesium carbonate, and 20 mol % of 2-*tert*-butylphenol.

Table 2. Rhodium-catalyzed allyl transfer from homoallyl alcohols **1** to acrylate esters **2**

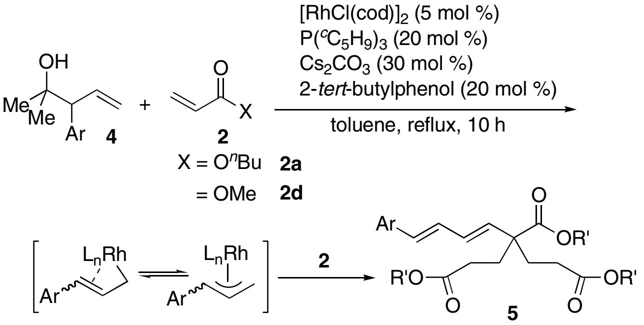


Entry	1	R	2	X	3, Yield[a] (%), *E*:*Z*
1	**1a**	Me	**2a**	O^{n}Bu	**3aa**, 70 (55), —
2	**1a**	Me	**2b**	O^{t}Bu	**3ab**, Trace
3	**1a**	Me	**2c**	NMe$_2$	**3ac**, (33), —
4	**1b**	Ph	**2a**	O^{n}Bu	**3ba**, 63 (50), 78:22
5	**1b**	Ph	**2d**	OMe	**3bd**, (70),[b] 81:19
6	**1c**	4-MeC$_6$H$_4$	**2a**	O^{n}Bu	**3ca**, 64 (54), 86:14
7	**1c**	4-MeC$_6$H$_4$	**2d**	OMe	**3cd**, 65 (58), 80:20
8	**1d**	3-CF$_3$C$_6$H$_4$	**2a**	O^{n}Bu	**3da**, 74 (42), 85:15
9	**1d**	3-CF$_3$C$_6$H$_4$	**2d**	OMe	**3dd**, 52 (47), 79:21

[a] Determined by ^{1}H NMR. Isolated yields are in parentheses. The *E*/*Z* ratios were tentatively assigned by comparing the ^{1}H NMR spectra of (*E*)- with (*Z*)-**3bd**.

[b] 1,4-Adduct, methyl 5-phenyl-5-hexenoate was obtained in 2% yield.

Table 3. Rhodium-catalyzed allyl transfer from homoallyl alcohols **4** to acrylate esters **2**

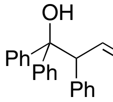


Entry	4	Ar	2[a]	5, Yield[b] (%)
1[c]	**4a′**	Ph	**2a**	**5aa**, 35
2	**4a**	Ph	**2a**	**5aa**, (55)
3	**4a**	Ph	**2d**	**5ad**, (67)
4	**4b**	4-MeC$_6$H$_4$	**2a**	**5ba**, 60 (58)
5	**4b**	4-MeC$_6$H$_4$	**2d**	**5bd**, 61 (55)
6	**4c**	4-MeOC$_6$H$_4$	**2a**	**5ca**, 61 (42)
7	**4c**	4-MeOC$_6$H$_4$	**2d**	**5cd**, (77)
8	**4d**	1-Naphthyl	**2a**	**5da**, 44
9	**4d**	1-Naphthyl	**2d**	**5dd**, 54

[a] For the reaction with **2a**, 4.0 equiv of **2a** was used while for **2d**, 12.0 equiv of **2d** was used.

[b] Determined by ^{1}H NMR. Isolated yields are in parentheses.

[c] Diphenyl-substituted homoallyl alcohol **4a′** was used.

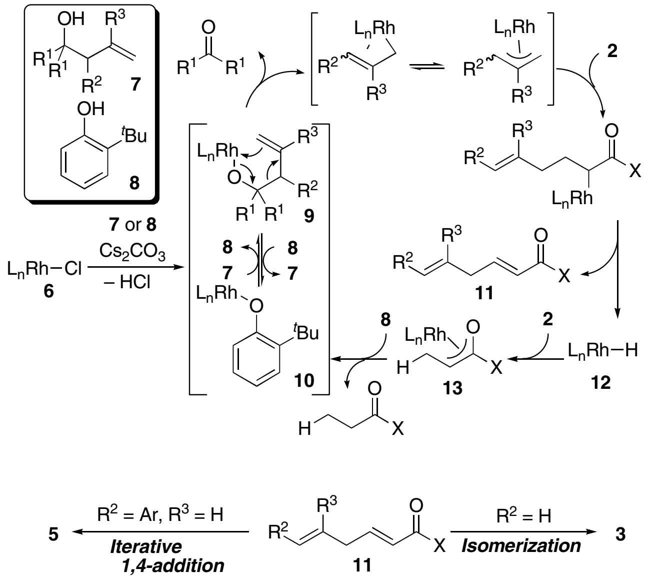


4a'

Next, we tested allyl transfer reactions of homoallyl alcohols **4** having an aryl group at the allylic position to acrylate esters **2a** and **2d** (Table 3). Homoallyl alcohol **4a′** was subjected to the standard conditions to furnish the unexpected triester **5aa**[4] in 35% (entry 1). In this case, dimethyl-substituted homoallyl alcohol **4a** gave better results (entries 2 and 3). The transfers of 4-methylphenyl- and 4-methoxyphenyl-substituted allyl moieties were also performed (entries 4–7). A naphthalene ring in **4d** decreased the yield slightly probably due to the steric factors (entries 8 and 9).

We are tempted to assume the following reaction mechanism (Scheme 1). Initial ligand exchange between a rhodium species **6** and homoallyl alcohol **7** or 2-*tert*-butylphenol (**8**) with the aid of cesium carbonate provides **9** or **10**. Alkoxides **9** and **10** would be in equilibrium. Retro-allylation of **9**[5] then occurs to generate σ-allylrhodium, the isomerization of which to π-allylrhodium would be reversible. Subsequent insertion of **2**[6] followed by β-H elimination provides **11** along with a rhodium hydride species **12**. In the case of homoallyl alcohol **7** ($R^2 = H$), isomerization of **11** proceeds in the same pots to produce conjugated 2,4-hexadienoate **3**. In contrast, with the use of homoallyl alcohol **7** ($R^2 = Ar$, $R^3 = H$), the corresponding 6-aryl-2,5-hexadienoate **11** undergoes iterative 1,4-addition to an excess of **2** to afford triester **5**.[7] Rhodium hydride **12** generated in situ reacts with **2** to give oxa-π-allylrhodium **13**. Subsequent protonolysis with **8** regenerates **10** to complete the catalytic cycle. Although the exact role of 2-*tert*-butylphenol (**8**) is not clear yet, it could work as a mediator converting oxa-π-allylrhodium **13** to **9**. Namely, the protonolysis of **13** with **8** would be much faster than that with **7**.[8]

In summary, we have extended the scope of the rhodium-catalyzed allyl transfer reaction. The allylrhodium was found to undergo addition to activated olefin.[9]



Scheme 1.

Further development of the retro-allylation system in other transformations catalyzed by transition metals is currently underway.

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Supplementary data

Supplementary data (experimental details and characterization data for new compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.04.039.

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