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Rhenium complex-catalyzed carbon-carbon formation of alcohols and organosilicon compounds

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ABSTRACT

The coupling reactions of allylic and benzylic alcohols and allyltrimethylsilane are efficiently catalyzed by a rhenium complex to give the corresponding 1,5-dienes and alkenes in moderate to good yields. Similarly, alcohols were coupled with ketene silyl acetals to form the corresponding esters.

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The Lewis acid mediated and catalyzed coupling reaction of various substrates with organosilicon compounds is a reliable and widely used method for constructing carbon-carbon bonds in organic synthesis. The use of inexpensive and readily available compounds, such as alcohols, is highly desirable for the reactions, especially from the view point of the sustainable chemistry. However, catalytic substitution of the hydroxy group in alcohols is difficult due to their poor leaving ability, which requires equivalent or excess amounts of a Lewis acid. Recently, the Lewis acid-catalyzed substituted reaction of alcohols with organosilicon compounds has been developed; however, there are some drawbacks of these methods; (i) limitation of the substrates, (ii) instability under a moist or air condition, and (iii) the use of excess amounts of the allylsilane (1.5 or 2.0 equiv.).[1–5]

We recently reported that $ReX(CO)_5$ (X = Cl or Br) serves as a catalyst for the α-alkylation of enol acetates with alcohols giving the corresponding α-alkylated carbonyl compounds.[6] Based on the continuous studies of the direct conversion of alcohols using a rhenium catalyst, we discovered the rhenium complex-catalyzed allylation of allylic and benzylic alcohols and their derivatives with an allylsilane (Scheme 1).[7–10] In addition, alcohols were also coupled with ketene silyl acetals to give the corresponding esters.[11]

We first investigated the effects of the rhenium complex, reaction temperature and solvent on the coupling reaction of 1,3-diphenylprop-2-en-1-ol (**1a**) and allyltrimethylsilane (**2a**) (Table 1). When **1a** and one equivalent amount of **2a** were stirred with a catalytic amount of $ReBr(CO)_5$ (5 mol%) in a 1,2-dichloroethane solvent under an atmosphere of nitrogen at 80 °C for 2 h, the coupling reaction of **1a** and **2a** proceeded to give 1,3-diphenyl-1,5-hexadiene (**3a**) in 90% yield (Entry 1). The yield of **3a** was improved by using a small excess amount of **2a**, and **3a** (1.2 equiv.) was obtained in 96% yield (Entry 2). Even when the reaction was carried out under an air atmosphere, the coupling reaction proceeded to give **3a** in 94% yield (Entry 3). For the lower reaction temperatures (60 and 40 °C), the yield of **3a** significantly decreased (Entries 4 and 5). When toluene, hexane, and 1,4-dioxane were used as the solvent, the reaction occurred to give **2a** in 25–80% yields (Entries 6–8). In the case of THF, acetonitrile and DMF, the reaction did not proceed at all (Entries 9–11). The use of CH_2ClCH_2Cl as the solvent led to the highest yield of **2a** (Entry 2). When $ReCl(CO)_5$ was used instead of $ReBr(CO)_5$ as the catalyst, **3a** was obtained in 94% yield (Entry 12). In the case of other rhenium complexes, such as $ReCl_5$ and Re_2O_7, **3a** was formed in 73 and 67% yields; however, $Re_2(CO)_{10}$ hardly exhibited any catalytic activity for the reaction (Entries 13–15).

The rhenium complex is a useful catalyst for the synthesis of 1,5-dienes by the coupling reaction of allylic alcohols and allyltrimethylsilane (**2a**). These results are shown in Table 2.[12] For the reaction of the 1,3-diaryl substituted allyl alcohols bearing electron-donating groups on both aromatic rings, such as 1,3-bis(4-methylphenyl)-, 1,3-bis(3-methylphenyl)-, and 1,3-bis(2-methylphenyl)-prop-2-en-1-ol, 1,3-diaryl substituted 1,5-hexadienes, **3b**, **3c**, **3d**, were formed in 78, 83, and 87% yields,

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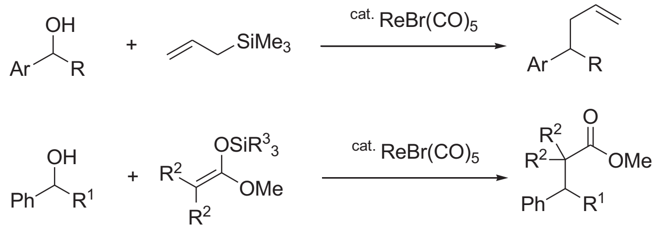


Scheme 1.

respectively (Entries 2–4). However, for the reaction of 1,3-bis(4-methoxyphenyl)-prop-2-en-1-ol bearing stronger electron donating group than the methyl group on the aromatic ring, the yield of 1,5-diene, **3e**, was low due to the formation of complicated by-products (Entry 5). In the case of 1,3-bis(4-chlorophenyl) prop-2-en-1-ol, in which the electron withdrawing group was substituted on both aromatic rings, 1,3-di(4-chlorophenyl)-1,5-diene, **3f**, was obtained in 84% yield (Entry 6). For the reaction of 3-(4-methylphenyl)-1-phenylprop-2-en-1-ol bearing two different aryl groups on the allyl alcohol, the mixture of 1-(4-methylphenyl)-3-phenyl-1,5-hexadiene (**3g**) and 3-(4-methylphenyl)-1-phenyl-1,5-hexadiene (**3g′**) (**3g**:**3g′** = 24:41) was formed in 65% yield (Entry 7). When 1-(4-methylphenyl)-3-phenylprop-2-en-1-ol was allowed to react with **2a**, the ratio of **3 g** and **3 g’** was almost the same as that of the reaction of 3-(4-methylphenyl)-1-phenylprop-2-en-1-ol (Entry 8). This tendency was observed for the reaction of various allylic alcohols (Entries 9–14). For the reaction of 3-phenylprop-2-en-1-ol, the 1,5-diene, **3e**, was not obtained due to the formation of complicated by-products (Entry 15).

The allylation of the other alcohols with allyltrimethylsilane (**2a**) was examined, and these results are shown in Scheme 2. Primary, secondary, and tertiary benzylic alcohols were efficiently coupled with **2a** to give the corresponding alkenes in 52, 75, 86, and 95% yields, respectively. Unfortunately, a simple aliphatic alcohol, such as 2-octanol, was not applicable for the rhenium-catalyzed reaction system.

The allylation of alcohol with various allylic silane was examined, and these results are shown in Scheme 3. When 1,3-diphenylprop-2-en-1-ol was treated with 2-methyl-3-trimethylsilyl-1-propene, the coupling reaction proceeded smoothly to give the corresponding coupling product, (*E*)-5-methyl-1,3-diphenyl-1,5-hexadiene (**3u**), in 95% yield. For the reaction of 1-phenyl-3-trimethylsilyl-1-propene, the diphenylmethanol was selective coupled with the allylic silane to give the 3,4,4-triphenyl-1-butene (**3v**) without the formation of 1,4,4-triphenyl-1-butene.

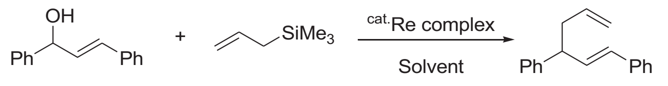
The reactions of alcohol derivatives, such as ether and ester, and allyltrimethylsilane (**2a**) were next examined and these results are shown in Scheme 4. When bis(diphenylmethyl) ether (**4a**) (0.10 mmol) was treated with a 2.4 equivalent amount of **2a**, 4,4-diphenyl-1-butene (**3r**) was obtained in 0.18 mmol. This result shows that both alkyl groups on the ether are efficiently used during the reaction. The ester **4b** was also allylated by **2a** to give **3r** in 84% yield along with the formation of benzoic acid (79%).

The rhenium complex also acts as a catalyst for the coupling reaction of diphenylmethanol and 1,3-diphenylprop-2-en-1-ol and ketene silyl acetal to produce the corresponding esters, **5a**, **b**, in 84 and 70% yields, respectively (Scheme 5). The α, α, α-trisubstituted ester **5c** was efficiently produced by this rhenium catalytic method.

To obtain information about the reaction pathway regarding the coupling of alcohol and trimethylallylsilane, the time-dependence of the product was followed by GC analysis at the appropriate time intervals. In the case of 1-phenylethanol, at the early stage of the reaction, the GC analysis showed the formation of bis(1-phenylethyl)ether. In contrast, for the reaction of 1,3-dipehylprop-2-ene-1-ol, the formation of the dehydration dimerized product was not observed. Based on these results, we proposed the following two reaction pathways.[13] The decarbonylation of $ReBr(CO)_5$ to form $ReBr(CO)_4$, which is the coordinative unsaturated 16-electron complex, is the first step of the catalytic reaction.[14] For the reaction of 1-phenylethanol, the coordination of rhenium species to the

Table 1

Reaction of 1,3-diphenylprop-2-en-1-ol (**1a**) and allyltrimethylsilane (**2a**).[a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Temp (°C)	Yield (%)[b]
1[c]	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	90
2	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	96 (92)
3[d]	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	94
4	$ReBr(CO)_5$	CH_2ClCH_2Cl	60	16
5	$ReBr(CO)_5$	CH_2ClCH_2Cl	40	16
6	$ReBr(CO)_5$	Toluene	80	80
7	$ReBr(CO)_5$	C_6H_{14}	80	25
8	$ReBr(CO)_5$	1,4-dioxane	80	35
9	$ReBr(CO)_5$	THF	80	0
10	$ReBr(CO)_5$	CH_3CN	80	0
11	$ReBr(CO)_5$	DMF	80	0
12	$ReCl(CO)_5$	CH_2ClCH_2Cl	80	94
13	$ReCl_5$	CH_2ClCH_2Cl	80	73
14[e]	Re_2O_7	CH_2ClCH_2Cl	80	67
15[e]	$Re_2(CO)_{10}$	CH_2ClCH_2Cl	80	15

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), Re catalyst (5 mol%), solvent (5 mL), 2 h under an atmosphere of N_2.

[b] GLC yield. The number in parenthesis shows the isolated yield.

[c] **2a** (0.20 mmol) was used.

[d] The reaction was carried out under an air atmosphere.

[e] Re catalyst (2.5 mol%) was used.

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