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

Rui Umeda,^a Toshifumi Jikyo,^a Kazuki Toda,^a Issey Osaka^b and Yutaka Nishiyama^a*

^a Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan
^b Center for Nano Materials and Technology, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292, Japan

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ABSTRACT

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Keywords: Rhenium Alcohols Allylsilane Alkenes The coupling reactions of allylic and benzylic alcohols and allytrimethylsilane 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.).



We recently reported that $\text{ReX}(\text{CO})_5(\text{X} = \text{Cl or Br})$ 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 complexcatalyzed 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 1,3diphenylprop-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 CH₂ClCH₂Cl 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 ReCl₅ 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).

* Corresponding author. Tel.: +81 6 6368 0902; fax: +81 6 6339 4026; e-mail: nishiya@kansai-u.ac.jp

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| Table 1. Reaction of 1,3 | 3-diphenylprop-2-en-1-ol (1a) and |
|---------------------------|-----------------------------------|
| allyltrimethylsilane (2a) |) ^a |

| (|)н Далан + | SiMe ₃ | cat.Re complex | |
|-----------------|------------------------------------|--------------------------------------|----------------|----------------|
| Ph | Ph | // ~ - | Solvent | Ph |
| | 1a | 2a | | 3a |
| Entry | Catalyst | Solvent | Temp (°C) | Yield $(\%)^b$ |
| 1^c | ReBr(CO) ₅ | CH ₂ ClCH ₂ Cl | 80 | 90 |
| 2 | ReBr(CO)5 | CH ₂ ClCH ₂ Cl | 80 | 96 (92) |
| 3^d | ReBr(CO) ₅ | CH ₂ ClCH ₂ Cl | 80 | 94 |
| 4 | ReBr(CO) ₅ | CH ₂ ClCH ₂ Cl | 60 | 16 |
| 5 | ReBr(CO) ₅ | CH ₂ ClCH ₂ Cl | 40 | 16 |
| 6 | ReBr(CO) ₅ | toluene | 80 | 80 |
| 7 | ReBr(CO) ₅ | $C_{6}H_{14}$ | 80 | 25 |
| 8 | ReBr(CO) ₅ | 1,4-dioxane | 80 | 35 |
| 9 | ReBr(CO) ₅ | THF | 80 | 0 |
| 10 | ReBr(CO) ₅ | CH ₃ CN | 80 | 0 |
| 11 | ReBr(CO) ₅ | DMF | 80 | 0 |
| 12 | ReCl(CO) ₅ | CH ₂ ClCH ₂ Cl | 80 | 94 |
| 13 | ReCl ₅ | CH ₂ ClCH ₂ Cl | 80 | 73 |
| 14^e | Re_2O_7 | CH ₂ ClCH ₂ Cl | 80 | 67 |
| 15 ^e | Re ₂ (CO) ₁₀ | CH ₂ ClCH ₂ Cl | 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 N₂. ^{*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.

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 1,3bis(2-methylphenyl)-prop-2-en-1-ol, 1,3-diaryl substituted 1,5hexadienes, 3b, 3c, 3d, were formed in 78, 83, and 87% yields, respectively (Entries 2-4). However, for the reaction of 1,3-bis(4methoxyphenyl)-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(4chlorophenyl)prop-2-en-1-ol, in which the electron withdrawing group was substituted on both aromatic rings, 1,3-di(4chlorophenyl)-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-(4methylphenyl)-1-phenyl-1,5-hexadiene (3g') (3g:3g' = 24:41)was formed in 65% yield (Entry 7). When 1-(4-methylphenyl)-3phenylprop-2-en-1-ol was allowed to react with 2a, the ratio of 3g and 3g' was almost the same as that of the reaction of 3-(4methylphenyl)-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 byproducts (Entry 15).

Table 2. Reaction of allylic alcohols **1** with allyltrimethylsilane $(2a)^a$



^{*a*}Reaction conditions: **1** (0.20 mmol), **2a** (0.24 mmol), ReBr(CO)₅ (5 mol%), CH₂ClCH₂Cl (5 mL) at 80 °C for 2 h under an atmosphere of N₂. ^{*b*}Isolated yield. ^{*c*}**2a** (0.4 mmol) was used. ^{*d*}CH₂ClCH₂Cl (2mL) was used.

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 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 1,3with 2-methyl-3diphenylprop-2-en-1-ol was treated trimethylsilyl-1-propene the coupling reaction proceeded smoothly to give the corresponding coupling product, (E)-5methyl-1,3-diphenyl-1,5-hexadiene (3u), in 95% yield. For the of 1-phenyl-3-trimethylsilyl-1-propene, reaction 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 timedependence 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 1,3dipehylprop-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 oxygen atom of ether, which is in situ formed by the intermolecular dehydration of alcohol, followed by the C-O bond cleavage of ether generates the stable carbocation.¹⁵ On the other hand, in the case of 1,3dipehylprop-2-ene-1-ol, the coordination of rhenium species to the oxygen atom of alcohols followed by the C-O bond cleavage of alcohols generates the stable carbocation.¹⁶ The carbocation was coupled with allyltrimethylsilane or ketene silyl acetal to give the corresponding alkenes or esters.

We report the rhenium complex-catalyzed coupling reaction of alcohols with allyltrimethylsilane or ketene silyl acetals to give the corresponding alkenes or esters. The application of the reaction and determining the reaction pathway are now in progress.

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16) We have investigated the reaction of the allylic alcohol, such as 1.3-dipehyl-prop-2-en-1-ol, with anisole in the presence of ReBr(CO)₅ catalyst, due to clear the formation of cation., the allylated product of anisole was formed in 45 % yield.

Highlights

A new catalytic ability of rhenium complex is described.

A new method for the formation of 1,5-diene and alkenes is developed.

Accepter A rhenium-catalyzed carbon-carbon bond formation of alcohols and organosilicons smoothly proceeded.