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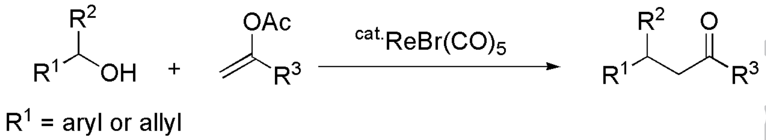

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Rhenium complex-catalyzed coupling reaction of enol acetates with alcohols

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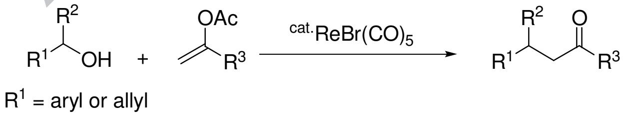
ABSTRACT

The reaction of enol acetates with alcohols in the presence of a catalytic amount of a rhenium complex, such as $ReBr(CO)_5$, produced the corresponding ketones and aldehydes in moderate to good yields. It was suggested that the preparation of an ether, an intermolecular dehydrated product, was the first step of the reaction.

The development of the transition metal-catalyzed carbon-carbon bond formation has significantly contributed to organic synthesis and many such methods have been reported. Although organic halides, alcohol derivatives having good leaving groups, such as tosylates and mesylates, or organometallic compounds were widely used as coupling partners for the carbon-carbon bond formation, the direct use of alcohols for the formation is limited, because of the poor leaving ability of the hydroxy unit and the decomposition of the catalysts and active intermediates.

The α-alkylation of carbonyl compounds is one of the fundamental transformations in organic synthesis, and various α-alkylation methods of carbonyl compounds have been developed.[1] Although the reaction of enolates or enamines with electrophiles was widely used for the alkylation of carbonyl compounds, the direct use of an alcohol as an electrophile remains a problem in organic synthesis. Recently, the direct α-alkylation of carbonyl compounds with alcohols has been developed.[2,3] Furthermore, alternative approaches via the catalytic transfer dehydrogenation of alcohols has been reported.[4,5] However, this is applicable only for the primary alcohols and required strong basic conditions.



Scheme 1.

Recently, it was shown that InI_3,[6] $GaBr_3$,[6] $La(OTf)_3$[7] and $Hf(OTf)_3$[7] catalyst are a novel catalyst for the preparation of α-alkylated carbonyl compounds by the reaction of enol acetates and alcohols. On these methods, there some disadvantages (i) limitation of the substrates, (ii) the use of toxic and expensive catalyst, (iii) unstable against moisture or air and (iv) the use of small excess amounts of reagent.

We and some Japanese groups developed $ReX(CO)_5$ (X = Cl or Br) can be used as a catalyst for organic reaction instead of various Lewis acid complexes.[8,9] On the continuous studies on the use of rhenium catalyst in organic synthesis, we now find that the $ReBr(CO)_5$ complex acts as the catalyst for the coupling reaction of enol acetates and alcohols to afford the ketones and aldehyde in moderate to good yields (Scheme 1). On the reaction, the reaction pathway, including the intermolecular dehydration of alcohol followed by the coupling reaction with enol acetates, was clearly disclosed.

In order to determine the optimized reaction conditions, we investigated the effects of the rhenium complex, reaction temperature and solvent on the reaction of 1-phenylethanol (**1a**) with isopropenyl acetate (**2a**) (Table 1). When 1-phenylethanol (**1a**) was allowed to react with isopropenyl acetate (**2a**) in the presence of a catalytic amount of $ReBr(CO)_5$ (5 mol%) in a 1,2-dichloroethane at 80 °C for 5 h, the coupling reaction of **1a** and **2a** smoothly proceeded to give 4-phenyl-2-pentanone (**3a**) in 88% yield (Entry 1). No reaction took place in the absence of the rhenium complex (Entry 2). For the lower reaction temperature (60 °C), the yield of **2a** was slightly decreased (Entry 3). Even when toluene and THF were used as the solvent, the reaction smoothly proceeded (Entries 5 and 6). In the case of acetonitrile, the reaction did not proceed (Entry 7). The use of CH_2ClCH_2Cl as the solvent led to the highest yield of **3a** (Entry 1). When $ReCl(CO)_5$ was used instead of $ReBr(CO)_5$ as the catalyst, **1a**

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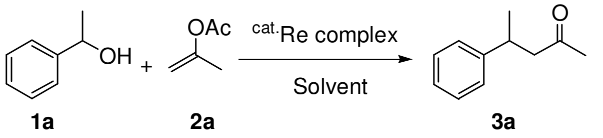
was coupled with **2a** to give **3a** in 53% yield (Entry 8). In the case of other rhenium complexes, such as $Re_2(CO)_{10}$, Re_2O_7, $ReCl_5$ and CH_3ReO_3, no formation of **3a** was observed (entries 9-12).[10]

Table 1. Reaction of 1-phenylethanol (**1a**) with isopropenyl acetate (**2a**)[a]



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

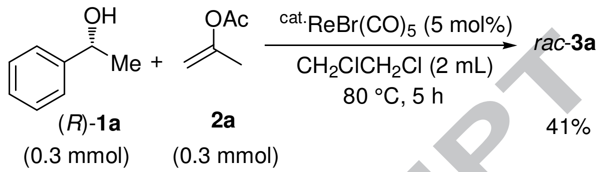
Entry	Catalyst	Solvent	Temp (°C)	Yield (%)[b]
1	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	88 (72)
2	none	CH_2ClCH_2Cl	80	0
3	$ReBr(CO)_5$	CH_2ClCH_2Cl	60	52
4	$ReBr(CO)_5$	CH_2ClCH_2Cl	100	86
5	$ReBr(CO)_5$	toluene	80	58
6	$ReBr(CO)_5$	THF	80	56
7	$ReBr(CO)_5$	CH_3CN	80	0
8	$ReCl(CO)_5$	CH_2ClCH_2Cl	80	53
9[c]	$Re_2(CO)_{10}$	CH_2ClCH_2Cl	80	0
10[c]	Re_2O_7	CH_2ClCH_2Cl	80	0
11	$ReCl_5$	CH_2ClCH_2Cl	80	0
12	CH_3ReO_3	CH_2ClCH_2Cl	80	0

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), Re catalyst (5 mol%), solvent (2 mL), 5 h.

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

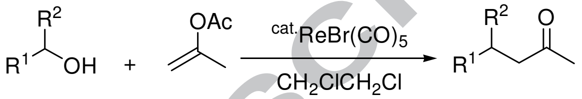
[c] Re catalyst (2.5 mol%).

The rhenium complex catalytic system is a quite efficient and general synthetic method of α-alkylated ketones by the reaction of alcohols and enol acetates. These results are shown in Table 2. The 1-aryl substituted ethanol bearing electron-donating groups on the aromatic ring, such as a 1-(4-methylphenyl)- and 1-(4-methoxyphenyl)-1-ethanol, gave the corresponding 4-aryl substituted 2-pentanones, **3b**,**c**, in 84 and 80% yields (Entries 1 and 2). For the reaction of 1-(4-chlorophenyl)-1-ethanol, the yield of ketone **3d** was low (Entry 3). In the case of the 1-aryl-1-ethanol substituted electron withdrawing group such as the nitro group, **3e** was not formed and 1-(4-nitrophenyl)ethyl acetate, which was a transesterfied product, was obtained in 82% yield (Entry 4). 1-(2-Methylphenyl)- and 1-(3-methylphenyl)ethanols gave 4-(2-methylphenyl)- and 4-(3-methylphenyl)-2-pentanones, **3f**,**g**, in 57 and 62% yields, respectively (Entries 5 and 6). 4-Phenyl-2-hexanone, 4,4-diphenyl-2-butanone, and 4,4,4-triphenyl-2-butanone, **3h**-**j**, were also prepared by the coupling reaction between isopropenyl acetate (**2a**) and 1-phenyl-propanol, benzhydrol, or triphenylmethanol (Entries 7-9). The preparation of the 4-naphthyl substituted 2-pentanones, **3k**,**l**, was successfully achieved using the rhenium catalytic system (Entries 10 and 11). Similarly, the coupling of 4-methoxybenzyl alcohol, a primary alcohol, with isopropenyl acetate (**2a**) proceeded to form 4-(4-methoxyphenyl-2-butanone (**3m**) in 56% yield together with uncharacterized products (Entry 12). The δ,γ-unsaturated ketones **3n** was obtained by the reaction of allylic alcohol such as 1-cyclohexene-3-ol with **2a** in 45 yields (entry 13). For the reaction of propargylic alcohol, the corresponding ketone was not formed due to the formation of various complicated products. In the case of tertiary alkyl alcohol, such as 5-butylnonan-5-ol, 5-butylnon-4-ene, dehydrated product, was formed in 51% yield. When (*R*)-(+)-1-phenylethanol (**1a**), chiral alcohol, was treated with **2a**, **3a** was formed with a racemic isomers (Scheme 2).

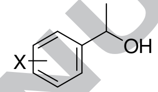
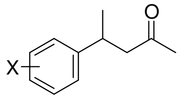
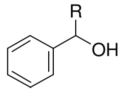
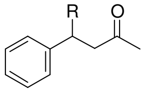
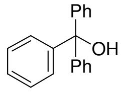
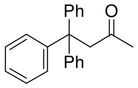
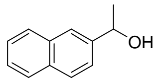
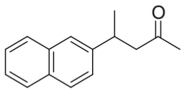
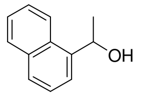
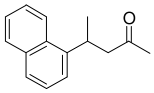
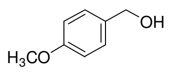
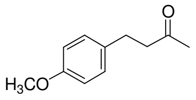
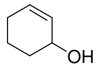
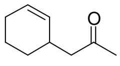


Scheme 2.

Table 2. Reaction of alcohols **1** with isopropenyl acetate (**2a**)[a]



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

Entry	Alcohol	Product	Yield (%)[b]
			
1	X = 4-CH_3 (**1b**)		84 (**3b**)
2	X = 4-CH_3O (**1c**)		80 (**3c**)
3	X = 4-Cl (**1d**)		38 (**3d**)
4	X = NO_2 (**1e**)		0[c] (**3e**)
5	X = 2-CH_3 (**1f**)		57 (**3f**)
6	X = 3-CH_3 (**1g**)		62 (**3g**)
			
7	R = C_2H_5		29 (**3h**)
8	R = Ph		83 (**3i**)
9	 (**1j**)		78 (**3j**)
10	 (**1k**)		63 (**3k**)
11	 (**1l**)		63 (**3l**)
12	 (**1m**)		56 (**3m**)
13			45 (**3n**)

(**1n**)

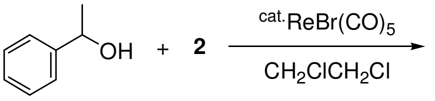
[a] Reaction conditions: alcohol (0.3 mmol), **2a** (0.3 mmol), $ReBr(CO)_5$ (5 mol%), CH_2ClCH_2Cl (2 mL), at 80 ºC for 5 h.

[b] Isolated yield.

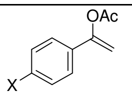
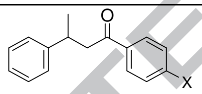
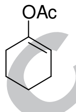
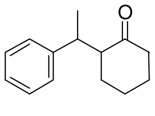
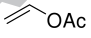
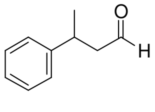
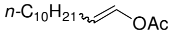
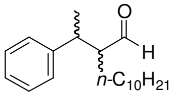
[c] 1-(4-nitrophenyl)ethyl acetate was formed in 82% yield.

Next, 1-phenylethanol (**1a**) was treated with various types of enol acetates **2** and these results are shown in Table 3. The rhenium-catalyzed reaction of the enol acetates **2**, which were derived from the acetophenones, and **1a** gave the corresponding coupling products **3o**-**s** (entries 1-5). It is interested to note that the yields of the products from the reaction with the electron withdrawing group substituted enol acetate were higher than those of the reaction with electron donating group substituted ones (entries 1-5). 2-(1-Phenylethyl)cyclohexanone (**3t**) was also prepared by the reaction of **1a** and cyclohexenyl acetate **2g** (entry 6). Similarly, the enol acetate **2h**, which was prepared from an aldehyde, gave the corresponding α-alkylated aldehyde **3u** (entry 7). The treatment of the mixture of *E*- and *Z*-isomers **2i** (*E/Z* = 1.5/1.0) and **1a** gave a mixture of regioisomers **3v** (*E/Z* = 1.5/1.0). It is interesting to note that when the mixture of *E*- and *Z*-isomers **2i** (*E/Z* = 1.0/7.2) was used as the enol acetate, the distribution of products **3v** (*E/Z* = 1.3/1.0) was almost same (entries 8 and 9).

Table 3. Reaction of 1-phenylethanol (**1a**) with enol acetates **2**[a]



1a

Entry	Enol acetates	Product	Yield (%)[b]
			
1	X = H (**2b**)		57 (**3o**)
2	X = 4-CH_3 (**2c**)		48 (**3p**)
3	X = 4-CH_3O (**2d**)		9 (**3q**)
4	X = 4-Cl (**2e**)		81 (**3r**)
5	X = 4-NO_2 (**2f**)		65 (**3s**)
6	 (**2g**)		58 (**3t**)
7	 (**2h**)		32 (**3u**)
	 (**2i**)		
8	*E* / *Z* = 1.5 / 1.0		43[c] (**3v**)
9	*E* / *Z* = 1.0 / 7.2		23[d] (**3v**)

[a] Reaction conditions: **1a** (0.3 mmol), enol acetates (0.3 mmol), $ReBr(CO)_5$ (5 mol%), CH_2ClCH_2Cl (2 mL), at 80 ºC for 5 h.

[b] Isolated yield.

[c] *Syn* / *anti* = 1.0 / 1.5. [d] *Syn* / *anti* = 1.0 / 1.3.

To obtain information about the reaction regarding the coupling of **1a** and **2a**, the time-dependence of the products was followed by GC measurement at the appropriate time intervals (Fig. 1). The GC analysis of the reaction product showed that bis(phenylethyl) ether (**4a**) was formed as the main product at an early stage of the reaction.[11] The yield of **4a** then gradually decreased and the yields of **3a** and α-methylbenzyl acetate (**5a**) increased. The acetate **5a** was gradually converted into **3a**. In fact, when bis(phenylethyl)ether (**4a**) (0.3 mmol) was treated with two equivalent amounts of **2a** (0.6 mmol) in the presence of the $ReBr(CO)_5$ catalyst, 4-phenyl-2-pentanone (**3a**) was formed in 77% yield (0.47 mmol) (Scheme 3). The conversion of **5a** into the **3a** was also achieved by the rhenium catalyst. Based on these results, it was suggested that both **4a** and **5a** were intermediates during the coupling reaction.

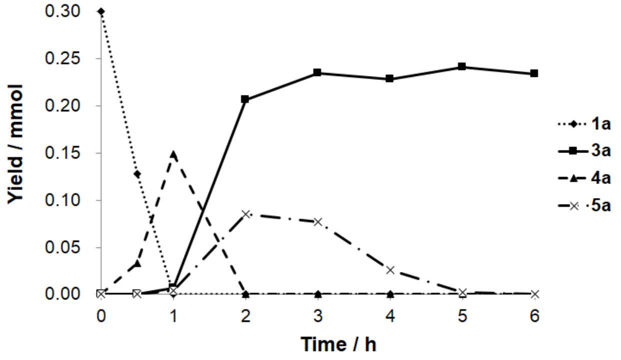
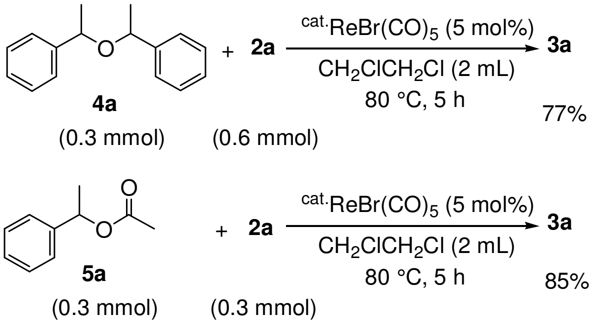
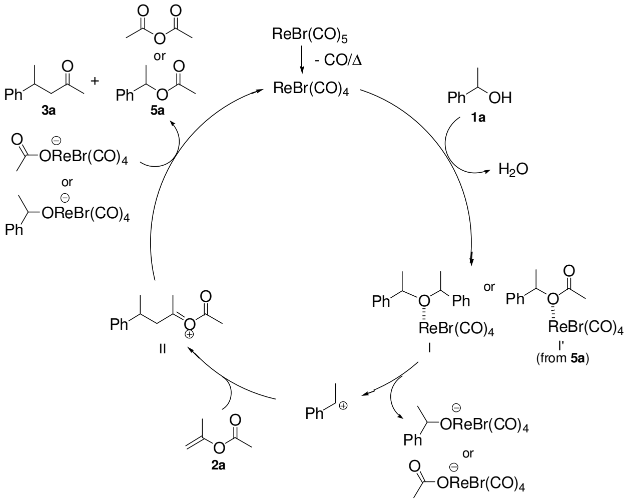


Figure 1. Time-dependence curves for the reaction of **1a** (0.3 mmol) with **2a** (0.3 mmol) in CH_2ClCH_2Cl (2 mL) at 80 ºC for 6 h



Scheme 3.

Based on the above observations, the plausible reaction pathways for the rhenium-catalyzed reaction are shown in Scheme 4. First, the decarbonylation of $ReBr(CO)_5$ to form $ReBr(CO)_4$, which is the coordinatively unsaturated 16-electron complex, is the first step of the catalytic reaction.[12] The C-O bond of bis(phenylethyl) ether (**4a**), which is in situ formed by the intermolecular dehydration of alcohol **1a**, is activated by the coordination of the rhenium species to increase the positive charge on the α-methylbenzyl group.[13] The addition of the benzilic cation generated from **I** to the C=C double bond of enol acetate **2a** followed by the deacetoxylation of **II** gave the corresponding ketone **3a** and α-methylbenzyl acetate (**5a**). The reaction of **5a** with **2a** was also easily occurred in the presence of the rhenium catalyst to afford **3a** as shown Scheme 4.



Scheme 4. A plausible reaction pathway

We exhibited that the rhenium complex-catalyzed reaction of enol acetates with alcohols gave the α-alkyl substituted carbonyl compounds. The application of the reaction and determining the reaction pathway are now in progress.

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13. We have shown that C-O bond of ether was effectively cleavage by rhenium complex. See ref 9e and 9f.

Supplementary Material

Supplementary data associated with this article can be found, in the online version, at