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Rhenium complex-catalyzed allylation of acetals with allyltrimethylsilane

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ABSTRACT

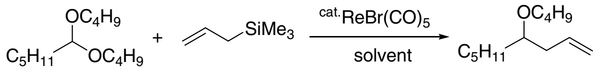
It was confirmed that the treatment of acetals with allyltrimethylsilane in the presence of a catalytic amount of the rhenium complex, $ReBr(CO)_5$, gave the corresponding homoallylic ethers in excellent to good yields.

The allylation of carbonyl compounds and their derivatives, such as acetals, with allyltrialkylsilane has been widely utilized as a method for the preparation of homoallylic alcohols and ethers.[1,2] Usually, these reactions require the presence of a Lewis or Brönsted acid promoter or catalyst. It is known that TMSOTf,[3] $(CH_3)_3SiI$,[4] trityl perchlorate,[5] diphenylboryl triflate,[5] montmorillonite,[6] $TiCp_2(CF_3SO_3)_2$,[7] trimethylsilyl bis(fluorosulfonyl)imide,[8] CF_3COOH,[9] SiO_2,[9] $BiBr_3$,[10] $TMSN(SO_2F)_2$,[11] $Sc(OTf)_3$,[12] $Bi(OTf)_3$,[13] $FeCl_3$,[14] $AlBr_3/CuBr$,[15] $Nb/AgClO_4$,[16] and sulfonic acid,[17] act as catalysts for the transformations; however, several of these methods suffer from drawbacks such as the involvement of compounds that are corrosive, difficult to handle or toxic and strictly anhydrous conditions.

We have recently shown the hitherto unknown ability of the rhenium complex, which is an air-stable and water-tolerant compound, to act as an efficient catalyst for the alkylation of arenes with alkyl halides,[18] the Mukaiyama aldol type reaction of carbonyl compounds with enol silyl ether and allylation of carbonyl compounds with allylstannane.[19] It is now found that the rhenium complex-catalyzed allylation of acetals with allyltrimethylsilane produced the corresponding homoallylic ethers in moderate to good yields (Scheme 1).[20]

To determine the optimized reaction conditions, hexanal dibutylacetal (**1**) was allowed to react with allyltrimethylsilane (**2**) under various reaction conditions, and these results are shown in Table 1. The yield of 4-butoxy-1-nonene (**3**) was affected by the solvent and rhenium complex used in the reaction. When chlorinated hydrocarbon solvents, such as 1,2-dichloroethane and chloroform, were used as a solvent, the allylation of **1** with **2** efficiently proceeded to give **3** in good yields, whereas the use of coordinating solvents, such as THF, acetonitrile or methanol, and the use of aromatic hydrocarbon solvents such as benzene and toluene caused a distinct decrease in the yield of **3** (entries 1–7). $ReBr(CO)_5$ and $ReCl(CO)_5$ showed a high catalytic activity for the reaction (entries 7 and 9). The rhenium carbonyl complexes, such as $Re_2(CO)_{10}$ and $Cp^*Re(CO)_5$, and manganese carbonyl complex $MnBr(CO)_5$ did not exhibit the same catalytic activity in the reaction (entries 10–12).

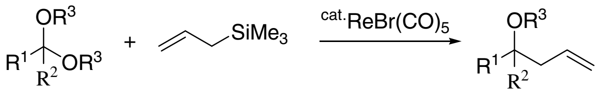
Table 1
Reaction conditions for the allylation of **1** with **2**[a]



1 **2** **3**

Entry	Re catalyst	Solvent	Yield[b] (%)
1	$ReBr(CO)_5$	Benzene	8
2	$ReBr(CO)_5$	Toluene	10
3	$ReBr(CO)_5$	THF	27
4	$ReBr(CO)_5$	CH_3CN	0
5	$ReBr(CO)_5$	CH_3OH	0
6	$ReBr(CO)_5$	$CHCl_3$	68
7	$ReBr(CO)_5$	CH_2ClCH_2Cl	100 (92)
8[c]	$ReBr(CO)_5$	CH_2ClCH_2Cl	82
9	$ReCl(CO)_5$	CH_2ClCH_2Cl	75
10	$Re_2(CO)_{10}$	CH_2ClCH_2Cl	Trace
11	$Cp^*Re(CO)_5$	CH_2ClCH_2Cl	Trace
12	$MnBr(CO)_5$	CH_2ClCH_2Cl	0

[a] Reaction conditions; **1** (1.0 mmol), **2** (1.2 mmol), $ReBr(CO)_5$ (0.1 mmol), and solvent (5 mL) at 60 °C for 5 h.
[b] GC yield. The number in the parentheses shows the isolated yield.
[c] $ReBr(CO)_5$ (0.025 mmol) was used for 24 h.



Scheme 1.

In order to determine the application of the allylation of acetals with allyltrimethylsilane (**2**), various acetals were reacted with **2** in the presence of a catalytic amount of $ReBr(CO)_5$ (10 mol %) at 60 °C for 5 h, and the results are shown in Table 2.[21] Hexanal dimethyl and diethyl acetals were converted into the corresponding

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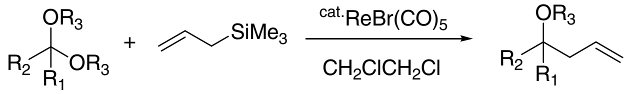
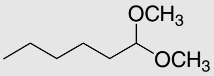
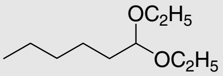
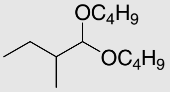
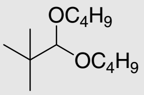
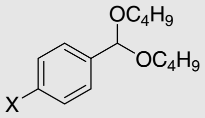
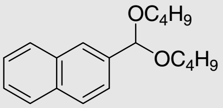
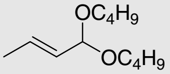
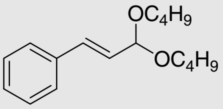
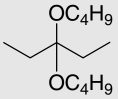
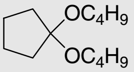
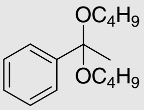
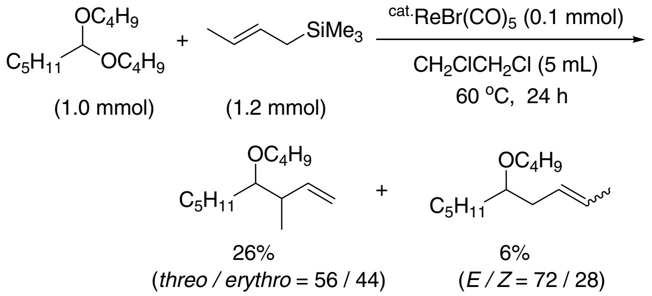
Table 2
Rhenium-catalyzed allylation of various acetals with allyltrimethylsilane[a]



Entry	Acetal	Yield[b] (%)
1		98 (98)
2		95 (82)
3		98 (84)
4		80 (71)
5	 X = H	97 (87)
6	$= OCH_3$	98 (91)
7	$= CH_3$	95 (85)
8	= Cl	95 (90)
9[c]	$= NO_2$	90 (85)
10		90 (86)
11		23 (12) (*E*/*Z* = 67/33)
12		98 (90) (*E*/*Z* = 79/21)
13		95 (88)
14		74 (65)
15[d]		62 (58)

[a] Reaction conditions: acetal (1.0 mmol), allyltrimethylsilane (1.2 mmol), $ReBr(CO)_5$ (0.1 mmol), and CH_2ClCH_2Cl (5 mL) at 60 °C for 5 h.
[b] GC yield. The number in parentheses shows the isolated yield.
[c] At 85 °C.
[d] $ReBr(CO)_5$ (0.2 mmol) was used for 24 h.



Scheme 2.

homoallylic ethers in the respective yields of 98% and 95% yields (entries 1 and 2). For 2-methylbutanal and pivalaldehyde dibutyl acetal, the allylation of the acetals with **2** efficiently proceeded under the same reaction conditions as that of the hexanal dibutyl acetal to give homoallylic butylethers in 98% and 80% yields, respectively (entries 3 and 4). Similarly, benzaldehyde and aromatic aldehyde dibutyl acetals, in which methoxy, methyl, chloro, and nitro groups were substituted on the aromatic ring, were allylated by allyltrimethylsilane to give the 4-butoxy-4-aryl-1-butene in excellent to good yields (entries 5–9). For the reaction of cinnamaldehyde dibutyl acetal, α,β-unsaturated aldehyde dibutyl acetal, 3-butoxy-1-phenyl-1,5-hexadiene was formed in 98% yield; however, in the case of crotonealdehyde, the yield of the allylated product was low (23%) due to the formation of various complicated by-products (entries 11 and 12). Dibutyl ketals derived from 3-pentanone and cyclopentanone were also allylated with **2** to give the 4-butoxy-4-ethylhex-1-ene and 1-allyl-1-butoxycyclopentanone in 95% and 74% yields (entries 13 and 14). In the case of the acetophenone dibutyl acetal, the yield of the allylated product was significantly decreased under the same reaction conditions as that of the 3-pentanone and cyclopentanone dibutyl ketals; however, the yield of product was improved by extending the reaction time (entry 15). When hexanal dibutylacetal (**1**) was allowed to react with 1-trimethylsilyl-2-butene, 4-butoxy-3-methyl-1-nonene was formed in 26% yield along with 5-butoxy-2-decene (6%) (Scheme 2).

Although we cannot show the reaction pathway for the rhenium-catalyzed allylation of acetals with allyltrimethylsilane in detail, the following reaction pathway was proposed for the reaction. It has already been reported that the coordinative unsaturated 16-electron complex was generated by the dissociation of carbon monoxide from $ReBr(CO)_5$ under toluene reflux conditions.[22] Based on this information, we suggested that the first step of the present allylation of acetals is the generation of a 16-electron rhenium species by the dissociation of carbon monoxide from the 18-electron rhenium complex, $ReBr(CO)_5$. The coordinative unsaturated rhenium species generated in situ acts as a Lewis acid for the allylation of acetal with allyltrimethylsilane.

In summary, it was found that a rhenium complex catalyzed the allylation of acetals with allyltrimethylsilane to give the corresponding homoallylic ethers in excellent to good yields. The application of the catalytic use of a rhenium complex in organic synthesis is now in progress.

Acknowledgments

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21. *Typical procedure*: 1,2-dichloroethane (5 mL) solution of acetal (1.0 mmol), allyltrimethylsilane (1.2 mmol) and ReBr(CO)$_5$ (0.1 mmol) was stirred with a magnetic stirrer bar vigorously under an atmosphere of nitrogen for 60 °C for 5 h. After the reaction, the reaction mixture was extracted with CHCl$_3$ (4 × 20 mL), and dried with MgSO$_4$ and then the solvent was removed using a rotary evaporator. Purification of the residue by column chromatography on silica gel produced the corresponding homoallylic ethers. The structure of the products was assigned by their ^{1}H and ^{13}C NMR, IR, and mass spectra.
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