Rhenium Complex as a Useful Catalyst for Acylative Cleavage of Ethers

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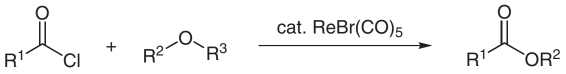
Abstract: It was found that a rhenium complex such as $ReBr(CO)_5$ acts as an efficient catalyst for the acylative cleavage of the carbon–oxygen bond of ethers with acyl chloride, giving the corresponding esters in moderate to good yields.

Key words: rhenium complex, ethers, acylation, esters, catalysis

The cleavage of a carbon–oxygen bond of ethers is a versatile reaction in organic synthesis and many methods have been developed.[1] Among them, the acylative cleavage of ethers with acyl chlorides is the attractive method for the preparation of esters. It is of great interested in the development of the catalytic method for the transformation of ethers into esters.[2]

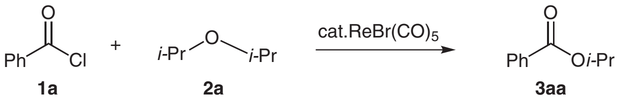
Recently, we have shown the hitherto unknown capacity of $ReBr(CO)_5$, which is an air-stable and a water-tolerant compound, as an efficient catalyst for the various carbon–carbon formation.[8,9] During the course of our study on the catalytic use of the rhenium complex, it was found that the $ReBr(CO)_5$ complex acts as the catalyst on the acylative cleavage of the carbon–oxygen bond of ethers with acyl chlorides giving the corresponding esters in moderate to good yields (Scheme 1).



Scheme 1

When benzoyl chloride (**1a**) was allowed to react with diisopropyl ether (**2a**) in the presence of a catalytic amount of $ReBr(CO)_5$ (2.5 mol%)[10] at 80 °C for two hours in 1,2-dichloroethane solvent, the acylative cleavage of carbon–oxygen bond of **2a** smoothly proceeded to give isopropyl benzoate (**3aa**) in 90% yield (entry 1 in Table 1).[11] To know the optimized reaction conditions, **1a** was treated with **2a** in the presence of the $ReBr(CO)_5$ catalyst under various reaction conditions and these results are shown in Table 1. The acylated product **3aa** was not obtained when the reaction was carried out under lower reaction temperatures (25 °C and 60 °C; entries 2 and 3). Even when the amount of $ReBr(CO)_5$ used as a catalyst was decreased; ester **3aa** was obtained in 87% yield (entry 4). Hexane and benzene were also available for the reaction (entries 5 and 6), whereas the use of coordinating solvents such as acetonitrile caused a distinct decrease in the yield of **3aa** (entry 7).

Table 1 Rhenium-Catalyzed Reaction of Diisopropyl Ether (**2a**) with Benzoyl Chloride (**1a**)[a]



Entry	Temp (°C)	Solvent	Yield (%)[b]
1	80	DCE	90
2	25	DCE	0
3	60	DCE	trace
4[c]	80	DCE	87
5	80	C_6H_{14}	81
6	80	C_6H_6	89
7	80	MeCN	0

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), $ReBr(CO)_5$ (2.5 mol%), and solvent (3.0 mL) for 2 h.
[b] GC yield based on **2a**.
[c] $ReBr(CO)_5$ (1.0 mol%) was used.

The representative results for the reaction of various acyl or aroyl chlorides with ethers are shown in Table 2.[11] On the reaction of dioctyl ether (**2b**) with **1a**, the yield of octyl benzoate (**3ab**) was only 8% yield; however, the yield of the ester **3ab** was improved by extending the reaction time and increasing the amount of the catalyst (entry 2 in Table 2). Allyl benzoate (**3ac**) was formed by the reaction of diallyl ether (**2c**) with benzoyl chloride (**1a**), in 83% yield (entry 3). For the reaction of dibenzyl ether (**2d**) with **1a**, although **2d** was completely consumed, the yield of benzyl benzoate (**3ad**) was low owing to the preparation of various unidentified side products (entry 4). In the case of diphenyl ether (**2e**), the acylative cleavage of **2e** did not proceed and **2e** was recovered (entry 5). For the reaction of the unsymmetric ethers such as *tert*-butyl methyl ether, *tert*-butyl ethyl ether, and *sec*-butyl ethyl ether (**2f**,**g**,**h**), respectively, it is interesting to note that the selective cleavage of the carbon–oxygen bond of these ethers **2f**,**g**,**h** proceeded to give methyl and ethyl benzoates **3af**,**ag**,**ah** in 72%, 76%, and 83% yields, respectively (entries 6–8). Similarly, the acylative cleavage of **2a** with various aroyl chlorides **1b**,**c**,**d** having electron-

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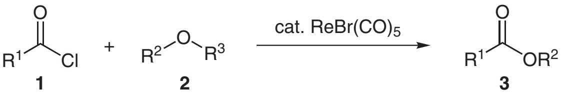
donating and electron-withdrawing groups on aromatic ring proceeded to give the corresponding esters **3ba**,**ca**,**da** in good yields (entries 9–11). For the reaction, there is no significant reactivity difference between the aroyl and acyl chlorides. The reaction of **2a** with octanoyl chloride (**1e**) and 2-ethylhexanoyl chloride (**1f**) proceeded to give the esters **3ea** and **3fa** in 95% and 88% yields, respectively (entries 12 and 13). When the 2,2-diethylheptanoyl chloride (**1g**), which have a sterically hindered group, was used as an acyl chloride, no acylative cleavage product **3ga** was formed (entry 14).

Table 2 Rhenium-Catalyzed Reaction of Ether **2** with Aroyl or Acyl Chloride **1**[a]



Entry	1	R^1	2	R^2	R^3	3	Yield (%)[b]
1	**1a**	Ph	**2a**	*i*-Pr	*i*-Pr	**3aa**	90
2[c,d]	**1a**		**2b**	C_8H_{17}	C_8H_{17}	**3ab**	43
3[c]	**1a**		**2c**	All	All	**3ac**	83
4	**1a**		**2d**	Bn	Bn	**3ad**	trace
5	**1a**		**2e**	Ph	Ph	**3ae**	0
6	**1a**		**2f**	Me	*t*-Bu	**3af**	72
7	**1a**		**2g**	Et	*t*-Bu	**3ag**	76
8	**1a**		**2h**	Et	*s*-Bu	**3ah**	83
9[e]	**1b**	4-MeC_6H_4	**2a**			**3ba**	82
10[e]	**1c**	4-$MeOC_6H_4$	**2a**			**3ca**	88
11[e]	**1d**	4-ClC_6H_4	**2a**			**3da**	94
12	**1e**	C_7H_{15}	**2a**			**3ea**	95
13[f]	**1f**	BuCHEt	**2a**			**3fa**	88
14	**1g**	$C_5H_{11}CEt_2$	**2a**			**3ga**	0

[a] Reaction conditions: **1** (0.6 mmol), **2** (0.5 mmol), $ReBr(CO)_5$ (2.5 mol%), and DCE (3.0 mL) at 80 °C for 2 h.

[b] GC yield based on **2**.

[c] For 5 h.

[d] $ReBr(CO)_5$ (12.5 mol%) was used.

[e] For 12 h.

[f] For 9 h.

For the reaction of dioctyl ether with **1a**, the formation of 1- and 2-chlorooctane and octenes were identified with GC analysis. In order to clarify the reaction pathway, a stoichiometric reaction of dioctyl ether (**2b**) with $ReBr(CO)_5$ was carried out at 80 °C; however, **2b** was recovered. Narasaka has already reported the rhenium complex catalyzed the Friedel–Crafts acylation of aromatic compounds having electron-donating groups such as methoxy and methyl with acyl chlorides giving the corresponding alkyl aryl ketones.[12] In the manuscript, they suggested that coordinatively unsaturated complex, $ReBr(CO)_4$, which was generated in situ the decarbonylation of CO coordinated with $ReBr(CO)_5$, acts as a Lewis acid catalyst. Thus, we proposed that the decarbonylation of CO coordinated with $ReBr(CO)_5$ to form the $ReBr(CO)_4$, is the first step at the catalytic reaction. Acyl and aroyl chlorides is coordinated to the $ReBr(CO)_4$ generated in situ. The activated species reacts with the oxygen of ether **2** and the elimination of chloride anion produces the oxonium salt. The cleavage of the carbon–oxygen bond of oxonium salt gave the ester **3**. On the other hand, the reaction pathway including the generation of acyl cation (RCO^+) and aroyl cation ($ArCO^+$), which are generated by the reaction of acyl and aroyl chlorides and $ReBr(CO)_4$, cannot be ruled out. Thus, we suggested that the nature of the eliminated groups played the important rule on the yields and the selectivity of the products **3**.

In summary, we developed a new catalytic method for the acylative and aroylative cleavage of the carbon–oxygen bond of ethers with acyl and aroyl chlorides giving the esters in moderate to good yields.

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(2) It was found that Lewis acids,[3] group 5 or 6 metal complexs,[4] metals such as Al[5] and Zn,[6] and iodine[7] can be used as a useful catalyst for the transformation. However, many of these methods involve some disadvantages (i) the use of toxic, expensive, and unstable agents, (ii) the formation of mixtures of products, (iii) low yields, and (iv) limitation of the substrates.

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(10) We also investigated the reaction of **1a** and **2a** using other rhenium complexes as a catalyst. The yields of ester **3aa** were in slightly lower compared to that of $ReBr(CO)_5$ (90%), $Re_2(CO)_{10}$ (71%), $MeReO_3$ (84%), $ReCl_5$ (74%), and Re_2O_7 (80%).

(11) **General Procedure**
A DCE (3.0 mL) solution of acyl chloride (0.6 mmol), ether (0.5 mmol), and $ReBr(CO)_5$ (2.5 mol%) was stirred under an atmosphere of nitrogen at 80 °C for 2 h. After the reaction was completed, H_2O was added to the reaction mixture and extracted with EtOAc. The organic layer was dried with $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated. Purification of the residue by silica gel column chromatography afforded ester. The structures of the products were assigned by their ^{1}H NMR, ^{13}C NMR, and mass spectra.

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