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Group 5 and group 6 metal halides as very efficient catalysts for acylative cleavage of ethers

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Abstract—Group 5 and 6 metal chlorides such as $MoCl_5$, WCl_6, $NbCl_5$ and $TaCl_5$ were found as very efficient catalysts for acylative cleavage of the C–O bond of ethers. Compared with conventional Lewis acid catalysts such as $ZnCl_2$, $AlCl_3$, $SnCl_4$ and $TiCl_4$, group 5 and 6 metal chlorides showed better results in the catalytic C–O bond cleavage of dibutyl ether with benzoyl chloride. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

$$R^1\text{-O-}R^2 \xrightarrow[\text{cat. MCl}_n]{\text{RCOCl}} \text{RCOOR}^1 \qquad (1)$$

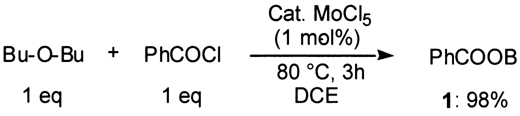
Cleavage of the C–O bond of ethers is important transformation in organic synthesis and a lot of methods have been already developed.[1–3] Among them, acylative cleavage of ethers is attractive, since it affords useful esters and it can be catalytic using Lewis acids such as $TiCl_4$ and $ZnCl_2$ and low-valent metal complexes such as $Mo(CO)_6$.[4–16] During the course of our study on $MoCl_5$, we found that it can be an efficient catalyst for the acylative C–O bond cleavage reaction of ethers.[17]

Furthermore, we found here that group 5 and 6 metal halides are more efficient catalysts compared with the known metal halides catalysts such as $TiCl_4$, $ZnCl_2$, $SnCl_4$ and $AlCl_3$. Here we would like to report the acylative cleavage of the C–O bond of ethers by using group 5 and 6 metal halides as efficient catalysts.

2. Results and discussion

2.1. Acylative cleavage of acyclic ethers catalyzed by $MoCl_5$

Dibutyl ether reacted with 1 equiv. of benzoyl chloride in dichloroethane (DCE) in the presence of 10 mol% of $MoCl_5$ at 80°C for 3 h to afford butyl benzoate in 95% yield as we reported preliminarily.[17] When 1 mol% of $MoCl_5$ was used as a catalyst, the yield was improved to 98% yield.



$$\underset{1\text{ eq}}{\text{Bu-O-Bu}} + \underset{1\text{ eq}}{\text{PhCOCl}} \xrightarrow[\text{80 °C, 3h}]{\text{Cat. MoCl}_5\ (1\text{ mol\%})} \underset{\mathbf{1}\text{: 98\%}}{\text{PhCOOBu}} \qquad (2)$$

DCE

This catalyst system is quite efficient and general for acyclic ethers as shown in Table 1. Dibutyl ether reacted with *n*-caproyl chloride at 80°C for 24 h, caproic acid *n*-butyl ester **2** was obtained in 96% (Table 1, entry 2). The lower reactivity of aliphatic acid chloride than aromatic acid chloride has been reported in the case of graphite.[18] In the reaction reported here, there is no significant difference between aromatic acid chloride and aliphatic acid chloride. When 2,2-dimethylpropionyl chloride, which has a sterically hindered *tert*-butyl group connected with the carbonyl group, was used instead of *n*-caproyl chloride, low yield of the ester **3** was obtained in the reaction with dibutyl ether. Dioctyl ether also reacted with benzoyl chloride and *n*-caproyl chloride to give octyl benzoate **4** and *n*-caproic acid *n*-octyl ester **6** in high yield, respectively (Table 1, entries 4 and 5).

It is interesting to note that some unsymmetrical ethers showed selective cleavage of the C–O bond. For example, allyl propyl ether reacted with caproyl acid chloride to give hexanoic acid propyl ester **7** (Table 1, entry 6). The formation of hexanoic acid allyl ester **8** was not observed in the reaction mixture. In contract, in the case of allyl trimethylsilyl ether, selective cleavage of the Si–O bond was observed (Table 1, entry 7), but the allyl–O bond was not cleaved. When ethyl trimethylsilyl ether reacted with

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Keywords: Lewis acids; C–O bond cleavage; ether.

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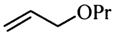
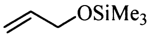
Table 1. Cleavage of the different ethers by using $MoCl_5$

$$R^1OR^2 \; + \; R^3COCl \xrightarrow[\text{DCE}]{MoCl_5 \text{ 0.1 eq}} R^3COOR^1 \; + \; R^2Cl$$

Entry	Ether	R^3COCl	Conditions	Product	Yield (%), GC (iso.)
1	Bu_2O	PhCOCl	80°C, 3 h	$PhCO_2Bu$ **1**	95 (75), 98[a]
2	Bu_2O	$C_5H_{11}COCl$	80°C, 24 h	$C_5H_{11}CO_2Bu$ **2**	96 (78)
3	Bu_2O	$(CH_3)_3CCOCl$	80°C, 24 h	$(CH_3)_3CCO_2Bu$ **3**	55 (32)
4	$C_8H_{17}OC_8H_{17}$	PhCOCl	80°C, 1 h	$PhCO_2C_8H_{17}$ **4**	88 (78), 98[a]
				$C_8H_{17}Cl$[b] **5**	72 (34)
5	$C_8H_{17}OC_8H_{17}$	$C_5H_{11}COCl$	80°C, 3 h	$C_5H_{11}CO_2C_8H_{17}$ **6**	94 (82)
				$C_8H_{17}Cl$[b] **5**	71 (56)
6		$C_5H_{11}COCl$	80°C, 1 h	$C_5H_{11}CO_2(CH_2)_2CH_3$ **7**	98 (81)
7		$C_5H_{11}COCl$	80°C, 3 h	$C_5H_{11}CO_2CH_2CH{=}CH_2$ **8**	75 (58)
8		PhCOCl	50°C, 3 h	$PhCO_2CH_2CH_3$ **9**	96 (91)
9	$CH_3OC(CH_3)_3$	PhCOCl	50°C, 1 h	$PhCO_2CH_3$ **10**	99 (76)
10	$PhCH_2OCH_2CH{=}CH_2$	PhCOCl	80°C, 1 h	$PhCO_2CH_2CH{=}CH_2$ **11**	75 (58)
11	$PhCH_2OCH_3$	PhCOCl	80°C, 3 h	$PhCO_2CH_3$ **10**	98 (82)
12	$PhCH_2OC(CH_3)_3$	PhCOCl	80°C, 1 h	$PhCO_2CH_2Ph$ **12**	61 (46)
				$PhCH_2Cl$[b] **13**	30 (10)
13	$CH_3OCH_2CH_2OCH_3$	PhCOCl	80°C, 24 h	$PhCO_2CH_2CH_2OCH_3$ **14**	38 (29)
14	$Cl(CH_2)_4O(CH_2)_4Cl$	PhCOCl	80°C, 24 h	$PhCO_2(CH_2)_4Cl$ **15**	99 (95)
				$Cl(CH_2)_4Cl$[b] **16**	98 (60)
15[c]	$CH_3O(CH_2)_2O(CH_2)_2OCH_3$	PhCOCl	80°C, 5 d	$PhCO_2(CH_2)_2Cl$ **17**	39 (35)
				$PhCO_2CH_3$ **10**	58 (53)

[a] GC yield when 0.01 equiv. of $MoCl_5$ was used.
[b] Isolated yields were in parentheses.
[c] 0.1 equiv. of $Zn(OTf)_2$ was used together with 0.1 eq. of $MoCl_5$ in this reaction.

aromatic acid chloride, we found the same selective cleavage of the Si–O bond selective cleavage. It afforded ethyl benzoate **9** in 96% (Table 1, entry 8). Similarly, methyl *tert*-butyl ether reacted with benzoyl chloride to give methyl benzoate **10** in 99% (Table 1, entry 9) i.e. the Bu^t–O bond in methyl *tert*-butyl ether was selectively cleaved.

When the reactivity of the R–O bond cleavage between alkyl, allyl, benzyl, trimethylsilyl and *tert*-butyl groups is compared, the order of the reactivity in this reaction is trimethylsilyl, *tert*-Bu>benzyl>allyl>alkyl. Trimethylsilyl and *tert*-Bu groups are sterically hindered groups and provide more stable cation species. The C–O bond of such groups is easily cleaved. Allyl and benzyl groups can stabilized the cationic or anionic species.[18] In addition, these groups can interact with transition metal center through their π-electrons. These results were consistent with the stoichiometric cleavage of the C–O bond of ethers, in which the alkyl group of greater electron-releasing power was selectively converted to halide.[19]

Table 2. Solvent effect on the C–O bond cleavage reaction of ethers

$$Bu_2O \; + PhCOCl \xrightarrow[\text{solvent, 3h}]{MoCl_5\text{, 0.1 eq}} PhCOOBu$$

Solvent	Temperature (°C)	GC yield (%)
Hexane	50	71[a]
Benzene	80	88[b]
CCl_4	50	60[c]
CH_2Cl_2	rt	17[d]
DCE	80	97
CH_3CN	80	10[e]

[a] For 24 h the yield reached to 99%.
[b] For 6 h the yield reached to 98%.
[c] For 24 h the yield reached to 81%.
[d] For 144 h the yield reached to 97%.
[e] After 48 h the yield was 29%, and no increase any more.

Interestingly, the present system using $MoCl_5$ is also suitable for the cleavage of polyether, for example, in the presence of 0.1 equiv. of $Zn(OTf)_2$, which can enhance the acidity of $MoCl_5$ acid, bis(2-methoxyethyl) ether was degradated to the corresponding esters. (Table 1, entry 15).

As for a solvent, dichloroethane was the best so far. Benzene or hexane was also available for this reaction as shown in Table 2. It was reported that acetonitrile is a good media for the C–O bond cleavage of aliphatic ethers in the presence of catalytic cobalt (II) chloride.[9] But in this system, acetonitrile did not provide good results for the C–O bond cleavage reactions.

2.2. Comparison of acylative cleavage of dibutyl ether by group 5 and 6 metal chlorides with that by other Lewis acids

Other group 6 metal halide such as WCl_6 also showed the similar reactivity for the same catalytic reaction and the butyl benzoate was formed in 96% yield under the same reaction conditions. Group 5 metal halides, $NbCl_5$ or $TaCl_5$ had similar reactivity as shown in Table 3. Interestingly, the comparison with other Lewis acid catalysts such as $AlCl_3$, $ZnCl_2$, $SnCl_4$, and $TiCl_4$ revealed that group 5 and 6 metal chlorides are more reactive than the usual Lewis acid catalysts under the conditions used here.

Table 3. Acylative cleavage of dibutyl ether catalyzed by different lewis acid

$$Bu_2O \quad + \quad PhCOCl \xrightarrow[\text{DCE, 80 }^{o}\text{C, 6h}]{\text{Lewis acid, 0.1 eq}} PhCOOBu$$

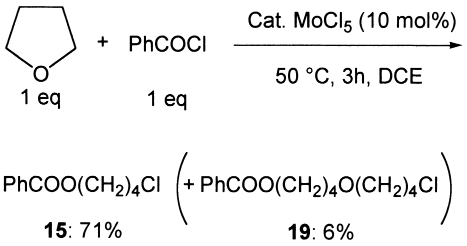
Lewis acid	$MoCl_5$	WCl_6	$NbCl_5$	$TaCl_5$	$AlCl_3$	$SnCl_4$	$TiCl_4$	$ZnCl_2$
GC yield (%)[a]	95	96	95 (98)	96	47 (77)	83 (90)	48 (77)	89 (93)

[a] The yield after stirring for 24 h are given in the parantheses.

2.3. The C–O bond cleavage of cyclic ethers catalyzed by group 5 and 6 metal halides

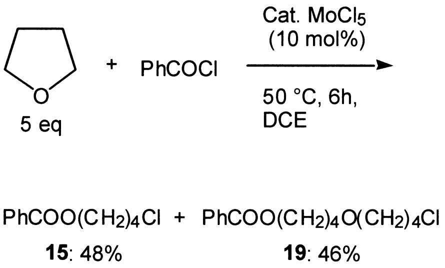
This catalyst system is also effective for the cleavage of the C–O bond of cyclic ethers. As shown in Table 4, cleavage reaction of different type of cyclic ethers proceeded in the presence of 10 mol% of $MoCl_5$ and produced the corresponding benzoates (Table 4, entries 1–6).

Trimethylene oxide reacted with benzoyl chloride to afford 83% of 3-chloropropyl benzoate **18**, and a reaction of tetrahydropyran with benzoyl chloride gave 5-chloropentyl benzoate **21** quantitatively (Table 4, entry 4). Interestingly, it was found that the C–O bond cleavage of a substituted cyclic ether such as 2-methyltetrahydrofuran proceeded with excellent selectivity. Only 4-chloropentyl benzoate **20** was obtained in 99% yield as a product. The C–O bond attached to the methyl substituent was cleaved. It is consistent with the fact that the C–O bond which gives more stable cation species is cleaved. Dioxane reacted with benzoyl chloride to afford 2-(2-chloroethoxy)ethyl benzoate **22** in 56% yield (Table 4, entry 5). Platinum-catalyzed acylative cleavage reaction of dioxane gave only low yield of the cleavage product as Fitch et al. reported.[20]



(3)

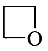
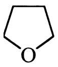
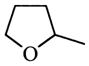
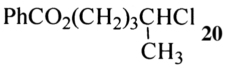
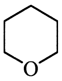
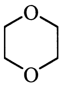
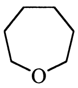
When the ratio of THF to benzoyl chloride was 5/1, the amount of 4-chlorobutoxybutyl benzoate **19** remarkably increased to 46% GC yield (32% isolated yield) as shown in Eq. (4). At 1/1 ratio, as shown in Eq. (3), **19** was formed only in 6% yield.



(4)

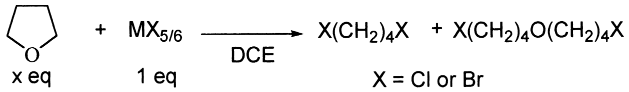
Table 4. Cleavage of the different cyclic ethers by using $MoCl_5$

$$(CH_2)_nO \quad + \quad PhCOCl \xrightarrow[\text{DCE}]{MoCl_5\text{ 0.1 eq}} PhCOO(CH_2)_nCl$$

Entry	Ether	Conditions	Product	Yield (%)[a]
1		rt, 3 h	$PhCO_2(CH_2)_3Cl$ **18**	83 (78)
2		50°C, 3 h	$PhCO_2(CH_2)_4Cl$ **15** $PhCO_2(CH_2)_4O(CH_2)_4Cl$ **19**	71 (56) 6 (4)
3		50°C, 3 h	 $PhCO_2(CH_2)_3\underset{CH_3}{CHCl}$ **20**	99 (96)
4		80°C, 3 h	$PhCO_2(CH_2)_5Cl$ **21**	99 (82) 96[b]
5		80°C, 168 h	$PhCO_2(CH_2)_2O(CH_2)_2CL$ **22**	56 (52)
6		80°C, 24 h	$PhCO_2CH_2CH_2Cl$ **17** $PhCO_2(CH_2)_6Cl$ **23**	6 (5) 65 (52)

[a] Isolated yields are in the parentheses.
[b] 0.01 equiv. of $MoCl_5$ was used.

Table 5. Chlorinative cleavage and dimerization of THF by $MX_{5/6}$



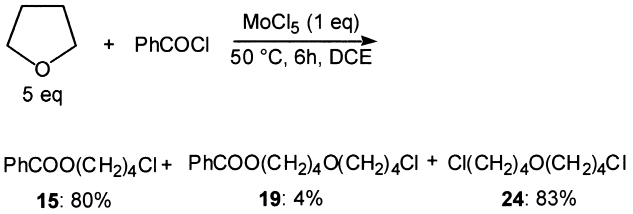
Entry	Lewis acid	*x* (equiv.)	Conditions	Yield[a]	
				Dihalobutane	Bishalobutylether
1	$MoCl_5$	1	50°C, 1 h	**16** 88 (70)	0
2	$MoCl_5$	4	50°C, 24 h	**16** 8 (6)	**24** 83 (76)
3	WCl_6	4	50°C, 48 h	**16** 10	**24** 123
4	$NbCl_5$	4	50°C, 48 h	**16** 5	**24** 82
5	$TaCl_5$	4	50°C, 48 h	**16** 10	**24** 88
6	WBr_5	4	50°C, 24 h	**25** 13 (6)[b]	**26** 30 (22)[c]

[a] GC yields(%), isolated yield are given in the parentheses. All the yields were based on $MX_{5/6}$.

[b] The yield of dibromobutane.

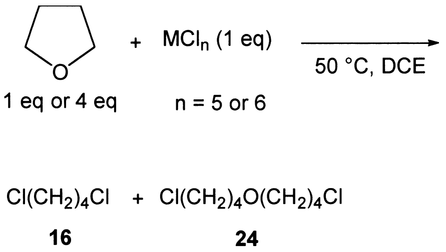
[c] The yield of bisbromobutylether.

This result prompted us to investigate the further reactions of THF in this system. As shown in Eq. (5), when 1 equiv. of $MoCl_5$ was used, bis(4-chlorobutyl) ether **24** was formed in 83% yield.



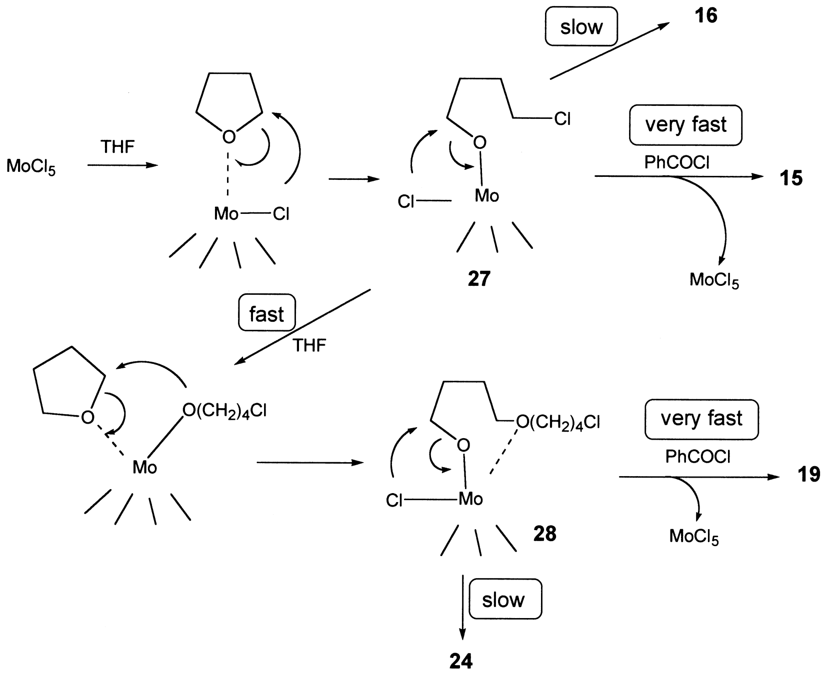
(5)

The product **24** was formed by the C–O bond cleavage of THF using $MoCl_5$ without benzoyl chloride. In order to investigate the C–O bond cleavage of THF without benzoyl chloride, the following reactions were carried out as shown in Eq. (6).

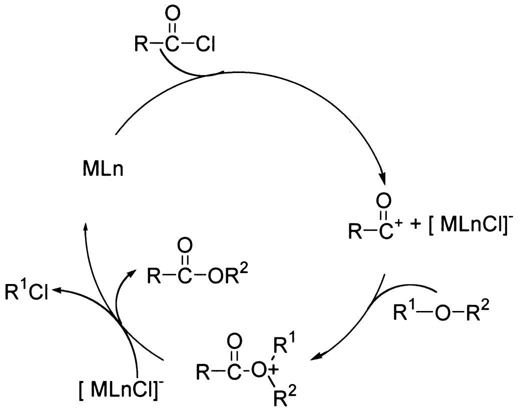


(6)

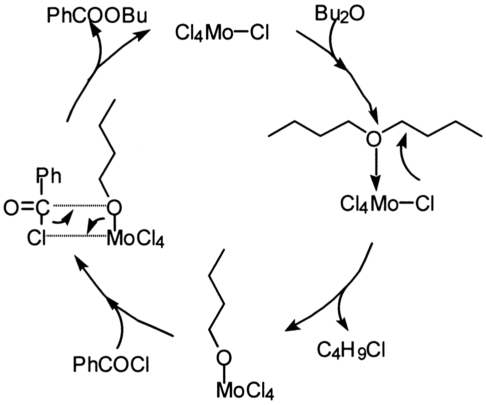
The results are shown in Table 5. When the ratio of THF to $MoCl_5$ was 1/1, only dichloride **16** was obtained in 88% yield. Interestingly, when the ratio of THF to $MoCl_5$ increased to 4/1, the yield of dichloride **16** remarkably decreased to 8% with increase of **24** to 83% yield. This clearly showed that the C–O bond of THF was cleaved by $MoCl_5$ without acid chloride and in the presence of additional THF, the resulting C–O bond cleaved species containing metal attacks the second THF to form dimerized compound. Judging from the high yield of **24**,



Scheme 1. Proposed mechanism for the formation of **15**, **16**, **19**, and **24** from THF and $MoCl_5$.



Scheme 2. Conventional mechanism.



Scheme 3. A proposed reaction mechanism of acylative cleavage of ethers.

oligomerization or polymerization did not proceed. Based on the results obtained for THF, the possible reaction mechanism is shown in Scheme 1.

THF coordinates to $MoCl_5$ in the first step. Coordination of THF to molybdenum chlorides has been reported and the structure of $[MoCl_4(THF)_2]$ is known,[21] although the Mo compound is not $MoCl_5$. One Cl of $MoCl_5$ attacks the carbon next to oxygen of THF to open the THF ring **27**, or the C–O bond cleavage occurs first and then the resulting cation species abstracts Cl from Mo. This type of chlorination followed by C–O bond cleavage has been reported for the reaction of anisole with $AlCl_3$.[19] If there is PhCOCl, esterification of the resulting alkoxy molybdenum **27** proceeds to give **15**. This is the main route in the catalytic reaction and this step is very fast compared with other steps as described below. If there is neither PhCOCl nor additional THF, the second Cl on the Mo of **27** attacks the carbon next to oxygen attached to Mo to afford **16**. This step is slow. Therefore, when enough THF or PhCOCl exists, the compound **16** is not formed. In the presence of additional THF, the alkoxy group of **27** attacks the second THF to afford **28**. Again, if there is PhCOCl, the esterification proceeds very fast to give **19**. The compound **28** does not react with the third THF, since the oxygen in the 4-(chlorobutoxy)butoxy group coordinates to Mo metal center to occupy the coordination site for the third THF. Without PhCOCl, chlorination proceeds to afford **24** as a product. This step also slow compared with the esterification reaction with PhCOCl.

It is usually believed that acylative C–O bond cleavage reaction proceeds via a cationic mechanism as shown in Scheme 2.[15,16,19,22] This mechanism involves the reaction of acid chloride with a catalyst first to generate RCO^+ ion. Addition of an ether to this cation gives an oxonium salt, $RCOO^+R^1R^2$, followed by cleavage of the C–O bond to give an ester. However, based on the observation described above for the C–O bond cleavage of THF, we believed that there exists a different mechanism which involves the C–O bond cleavage of THF in the presence of $MoCl_5$ without acid chloride.

In order to make this point clear, we carried out the following reaction of dioctyl ether with $MoCl_5$ at 80°C (without addition of any acid chloride in this stage). After stirring for 3 h, 1-chlorooctane (**5**) was obtained in 93%. Then, to this resulting mixture, benzoyl chloride was added and octyl benzoate (**4**) was obtained in 49% as shown in Eq. (7).

$$\underset{1\text{ eq}}{C_8H_{17}OC_8H_{17}} \xrightarrow[80\,^{\circ}C,\ 3h]{MoCl_5\ 1eq} \underset{\mathbf{5}:\ 93\%}{C_8H_{17}Cl} + [C_8H_{17}OMoCl_n] \quad \text{reaction mixture} \tag{7}$$

$$\xrightarrow[80\,^{\circ}C,\ 3h]{PhCOCl\ 1\ eq} \underset{\mathbf{4}:\ 49\%}{PhCO_2C_8H_{17}} + \underset{\mathbf{5}:\ 93\%}{C_8H_{17}Cl}$$

This clearly shows that dioctyl ether reacted with $MoCl_5$, and the C–O bond of dioctyl ether was cleaved to form 1-chlorooctane and $[C_8H_{17}OMoCl_n]$ complex. The intermediate could not be characterized but it can be assumed that then benzoyl chloride reacted with the molybdenum complex to give octyl benzoate. This mechanism is consistent with the observation in the acylative cleavage of C–O bond of ether described above. However, the conventional cation mechanism is not ruled out in this reaction.

Although the complex $[C_8H_{17}OMoCl_n]$ was not characterized yet, this type of cleavage has been observed in the reaction of anisole with aluminum chloride. Methyl chloride and phenol were isolated from the non-volatile residue.[19] It is known that THF coordinates to molybdenum (IV) by its ether oxygen to form tetrachlorobis(tetrahydrofuran)-molybdenum (IV) $[MoCl_4(THF)_2]$ complex.[21] It is interesting to note that Cl does not attack THF in the complex. However, $MoCl_5$ is very reactive toward THF probably due to its higher Lewis acidity. A proposed mechanism is shown in Scheme 3. The mechanism proposed here is quite different from the cationic mechanism which has been generally proposed for the catalytic acylative cleavage of the C–O bond of ethers. For example, in catalytic acylative cleavage of ethers with $FeCl_3$–Ac_2O and group 6 metal carbonyl derivatives,[15,16] a cation mechanism was proposed. The C–O bond of ethers can be cleaved only by metal halides in our system which is similar to stoichiometric C–O bond cleavage of ethers with Lewis acids. The role of the acid chlorides in the reactions reported here is not formation of the oxonium salt but providing Cl^- to Cl_4MoOR to regenerate $MoCl_5$ and esters.

3. Conclusions

In conclusion, high-valent group 5 and group 6 metal (Mo, W, Nb and Ta) halides provide a very convenient and efficient catalyst systems in the C–O bond cleavage reaction of ethers. Various acyclic and cyclic ethers were converted to the corresponding esters in high yields with high selectivity. A novel reaction mechanism was proposed for the ether cleavage reaction. The most significant features of this catalytic cycle are, alkoxy metal chloride [$ROMCl_n$] was formed as an important step, and then this species reacted with acid chloride to afford esters. This mechanism is quite different from the conventionally accepted mechanism which involves the formation of RCO^+ as a key step for acylative cleavage of ethers.

4. Experimental

All reactions were carried out under nitrogen. Metal chlorides were handled under nitrogen atmosphere. Solvents were dried and distilled under nitrogen. Other chemicals, purchased from Aldrich Inc. and TCI Co. Ltd. or Kanto Chemical Co. Ltd., were used without further purification.

^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ (containing 1% TMS) solution at 25°C on Bruker ARX NMR spectrometer. GC analysis was performed on Shimadzu GC-14A equipped with a fused silica capillary column Shimadzu CBP1-M25-O25 and Shimadzu C-R6A-Chromatopac integrator. GC analysis was carried out using hydrocarbon as internal standards.

4.1. A representative procedure for the catalytic ether cleavage reaction

To a mixture of molybdenum chloride (0.1 mmol, 27 mg) and DCE (5 ml) were added dibutyl ether (1 mmol, 130 mg) and benzoyl chloride (1 mmol, 141 mg). The reaction mixture was stirred at 80°C for 3 h. GC analysis of the resulting mixture after hydrolysis showed the formation of butyl benzoate in 95% yield. The reaction mixture was then quenched and extracted with diethyl ether (3×30 ml). The extract was washed with water, $NaHCO_3$ (20% aqueous solution), water, and brine and then dried over anhydrous $MgSO_4$. Filtration, evaporation, and column chromatography on silica gel with hexane/ether (30/1, v/v) as eluent afforded the butyl benzoate **1** as a colorless liquid (134 mg, 75%). The compound was easily identified by comparing their ^1H and ^{13}C NMR spectra with a reference.[23]

The ^1H and ^{13}C NMR spectra of the following ether cleavage products are identical with the references: octyl benzoate **4**,[24] 1-chlorooctane **5**,[25] caproic acid octyl ester **6**,[24] methyl benzoate **10**,[23] benzyl benzoate **12**,[26] benzoyl chloride **13**,[27] 2-methoxy ethyl benzoate **14**,[26] 4-chlorobutyl benzoate **15**,[28] 1,4-dichlorobutane **16**,[28] 4-chloropentyl benzoate **20**,[15] and 1,4-dibromobutane **25**.[28]

4.1.1. Caproic acid *n*-butyl ester (2).[29] Ester **2** was obtained in 78% yield (269 mg) from dibutyl ether (2 mmol) and caproic acid chloride (2 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/EtOAc, 20/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J=7.5 Hz, 3H), 0.94 (t, J=7.4 Hz, 3H), 1.22–1.85 (m, 10H), 2.29 (t, J=7.6 Hz, 2H), 4.07 (t, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.72, 13.92, 19.17, 22.33, 24.73, 30.73, 31.35, 34.39, 64.12, 174.05; HRMS calcd for $C_{10}H_{21}O_2$ (MH^+) 173.1542, found 173.1544.

4.1.2. 2,2-Dimethylpropionic acid butyl ester (3).[30] Ester **3** was obtained in 32% yield (102 mg) from dibutyl ether (2 mmol) and 2,2-dimethylpropionic acid chloride (2 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/Et_2O, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.84 (t, J=7.4 Hz, 3H), 1.20 (s, 9H), 1.39 (tq, J=7.3, 7.6 Hz, 2H), 1.60 (tt, J=6.6, 7.5 Hz, 2H), 4.06 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.75, 19.19, 27.22, 30.72, 38.75, 64.19, 178.68; HRMS calcd for $C_9H_{18}O_2$ (M^+) 158.1307, found 158.1307.

4.1.3. Caproic acid propyl ester (7).[31] Ester **7** was obtained in 81% yield (128 mg) from allyl propyl ether (1 mmol) and caproic acid chloride (1 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/Et_2O, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J=6.6 Hz, 3H), 0.94 (t, J=7.4 Hz, 3H), 1.26–1.32 (m, 4H), 1.59–1.68 (m, 4H), 2.30 (t, J=7.5 Hz, 2H), 4.03 (t, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 10.37, 13.88, 21.98, 22.30, 24.68, 31.30, 34.33, 65.78, 173.99; HRMS calcd for $C_9H_{18}O_2$ (M^+) 158.1307, found 158.1306.

4.1.4. Caproic acid allyl ester (8).[32] Ester **8** was obtained in 58% yield (181 mg) from allyl trimethylsilyl ether (2 mmol) and caproic acid chloride (2 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/ether, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, J=6.8 Hz, 3H), 1.25–1.34 (m, 4H), 1.58–1.67 (m, 2H), 2.32 (t, J=7.5 Hz, 2H), 4.56 (d, J=5.8 Hz, 2H), 5.22 (d, J=10.4 Hz, 1H), 5.30 (d, J=17.2 Hz, 1H), 5.90 (ddt, J=10.4, 17.1, 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.90, 22.31, 24.64, 31.30, 34.25, 64.92, 118.07, 132.34, 173.55; HRMS calcd for $C_9H_{16}O_2$ (M^+) 156.1150, found 156.1149.

4.1.5. Ethyl benzoate (9).[33] Ester **9** was obtained in 91% yield (137 mg) from ethyl trimethylsilyl (1 mmol) and benzoic acid chloride (1 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/Et_2O, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.40 (t, J=7.2 Hz, 3H), 4.38 (q, J=7.2 Hz, 2H), 7.40–7.45 (m, 2H), 7.52–7.57 (m, 1H), 8.03–8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.29, 60.90, 128.26, 129.49, 130.46, 132.76, 166.60.

4.1.6. Allyl benzoate (11).[34] Ester **11** was obtained in 58% (188 mg) from benzyl allyl ether (2 mmol) and benzoic acid chloride (2 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/Et_2O, 40/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 4.83 (d, J=5.6 Hz, 2H), 5.29 (dd, J=10.3, 1.0 Hz, 1H), 5.42 (dd, J=17.2, 1.3 Hz, 1H), 6.04 (ddt, J=17.2, 10.5, 5.6 Hz, 1H), 7.44 (t, J=7.7 Hz, 2H), 7.56 (t, J=7.4 Hz, 1H), 8.07 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 65.54, 118.22, 128.37, 129.63, 130.13, 132.22, 132.99, 166.25.

4.1.7. 3-Chloropropyl benzoate (18).[35] Ester **18** was obtained in 78% yield (465 mg) from trimethylene oxide (3 mmol) and benzoic acid chloride (3 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/Et_2O, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 2.24 (tt, J=6.3, 6.6 Hz, 2H), 3.70 (t, J=6.5 Hz, 2H), 4.48 (t, J=6.0 Hz, 2H), 7.44 (t, J=7.5 Hz, 2H), 7.52–7.58 (m, 1H), 8.04 (d, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 31.77, 41.29, 61.69, 128.43, 129.59, 130.06, 133.08, 166.42.

4.1.8. 4-(4-Chlorobutoxy)butyl benzoate (19). Ester **19** was obtained in 32% yield (46 mg, the yield is based on PhCOCl) from THF (25 mmol) benzoic acid chloride (5 mmol) and $MoCl_5$ (0.5 mmol) as a colorless liquid (flash chromatography with a mixture of hexane/Et_2O, 30/1 and 20/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.63–1.91 (m, 8H), 3.42–3.50 (m, 4H), 3.57 (t, J=6.5 Hz, 2H), 4.35 (t, J=6.5 Hz, 2H), 7.41–7.46 (m, 2H), 7.53–7.58 (m, 1H), 8.03–8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.65, 26.37, 27.09, 29.54, 45.00, 64.80, 70.00, 70.31, 128.34, 129.55, 130.40, 132.87, 166.65; HRMS calcd for $C_{15}H_{21}ClO_3$ (M^+) 284.1179, found 284.1190.

4.1.9. 5-Chloropentyl benzoate (21).[9] Ester **21** was obtained in 82% yield (186 mg) from THP (1 mmol) and benzoic acid chloride (1 mmol) as a colorless oil (flash chromatography with a mixture of hexane/Et_2O, 20/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.54–1.65 (m, 2H), 1.78–1.93 (m, 4H), 3.57 (t, J=6.6 Hz, 2H), 4.34 (t, J=6.5 Hz, 2H), 7.44 (t, J=7.7 Hz, 2H), 7.54–7.61 (m, 1H), 8.04–8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.47, 28.06, 32.18, 44.78, 64.66, 128.37, 129.55, 130.35, 132.91, 166.62.

4.1.10. 2-(2-Chloroethoxy)ethyl benzoate (22)[36] and 2-chloroethyl benzoate (17).[37] Ester **22** was obtained in 52% yield (357 mg) from 1,4-dioxane (3 mmol) and benzoic acid chloride (3 mmol) as a colorless oil (flash chromatography with a mixture of hexane/Et_2O, 10/1), at the same time, ester **17** was isolated as a byproduct (55 mg, 10%). Data of **22**: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.65 (t, J=5.8 Hz, 2H), 3.81 (t, J=5.7 Hz, 2H), 3.87 (t, J=4.8 Hz, 2H), 4.49 (t, J=4.8 Hz, 2H), 7.45 (t, J=7.2 Hz, 2H), 7.54–7.61 (m, 1H), 8.07 (d, J=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 42.71, 63.95, 69.25, 71.30 128.37, 129.68, 129.98, 133.06, 166.53. Data of **17**: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.80–3.83 (m, 2H), 4.55–4.58 (m, 2H), 7.43–7.47 (m, 2H), 7.55–7.59 (m, 1H), 8.07 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 41.70, 64.46, 128.45, 129.61, 129.74, 133.28, 166.17.

4.1.11. 6-Chlorohexyl benzoate (23). Ester **23** was obtained in 52% yield (125 mg) from oxepane (1 mmol) and benzoic acid chloride (1 mmol) as a colorless oil (flash chromatography with a mixture of hexane/Et_2O, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.46–1.57 (m, 4H), 1.78 (tt, J=6.3, 7.1 Hz, 4H), 3.55 (t, J=6.7 Hz, 2H), 4.33 (t, J=6.6 Hz, 2H), 7.43–7.46 (m, 2H), 7.54–7.58 (m, 1H), 8.03–8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.42, 26.57, 28.59, 32.46, 44.98, 64.85, 128.35, 129.53, 130.38, 132.87, 166.66. HRMS calcd for $C_{13}H_{17}ClO_2$ 240.0917, found 240.0928.

4.1.12. Bis(4-chlorobutyl) ether (24).[38] Ether **24** was obtained in 70% yield (139 mg, the yield is based on $MoCl_5$ (1 mmol)) from THF (5 mmol) and benzoic acid chloride (1 mmol) as a colorless oil (flash chromatography with a mixture of hexane/Et_2O, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.71 (tt, J=6.2, 7.2 Hz, 4H), 1.86 (tt, J=6.8, 7.2 Hz, 4H), 3.43 (t, J=6.1 Hz, 4H), 3.57 (t, J=6.6 Hz, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.11, 29.58, 44.97, 69.98.

4.1.13. Bis(4-bromobutyl) ether (26).[38] Ether **26** was obtained in 25% yield (72 mg, the yield is based on WBr_5 (1 mmol)) from THF (4 mmol) as a colorless oil (flash chromatography with a mixture of hexane/Et_2O, 30/1). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.68–1.75 (m, 4H), 1.91–1.98 (m, 4H), 3.42–3.46 (m, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 28.29, 29.67, 33.77, 69.81.

4.2. Stoichiometric reaction of dioctyl ether with $MoCl_5$

To a mixture of molybdenum chloride (1.0 mmol, 270 mg) and DCE (5 ml) was added dioctyl ether (1 mmol, 242 mg). The reaction mixture was stirred at 80°C for 3 h. GC analysis of the resulting mixture sample after hydrolysis showed the formation of 1-chlorooctane in 93% GC yield. And then benzoyl chloride (1 mmol, 141 mg) was added, it was stirred for additional 3 h at 80°C. After that, the reaction mixture was quenched and extracted. The extraction was treated as shown in the representative procedure above, column chromatography on silica gel afforded the octyl benzoate ester (106 mg, 45%; GC yield: 49%) and 1-chlorooctane (97 mg, 65%; GC yield: 93%) as colorless liquid.

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