Molybdenum- and Rhenium-catalyzed Isomerization of Cyclopropanemethanols to Tetrahydrofurans

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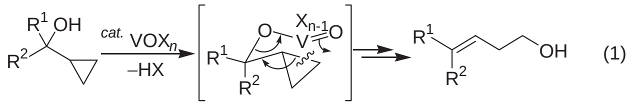
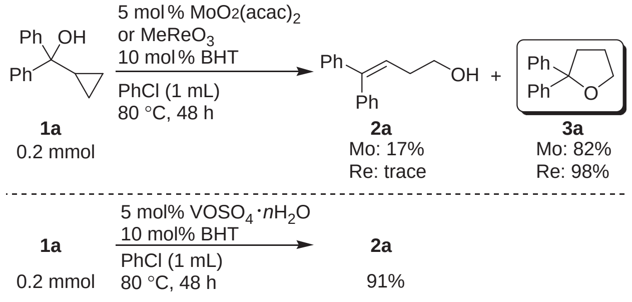
Molybdenum- and rhenium-complexes work as affective catalysts for isomerization of a variety of cyclopropanemethanols into the corresponding tetrahydrofurans in good to high yields. The reaction may proceed via 1) [3,3]sigmatropic rearrangement involving an oxo metal cyclopropanemethanolate accompanied by the C–C bond cleavage and 2) the metal-catalyzed intramolecular hydroalkoxylation of the initially produced homoallylic alcohols.

Transformation of cyclopropanes via C–C bond cleavage into a variety of organic compounds is a useful reaction in view of organic synthesis and many reactions have been reported.[1] Recently, we disclosed the vanadium-catalyzed isomerization of cyclopropanemethanols to homoallylic alcohols under atmospheric condition (Eq 1).[2] This reaction may proceed via [3,3]sigmatropic rearrangement of an oxovanadium cyclopropanemethanolate intermediate, similar to vanadium-catalyzed 1,3-allylic transposition of allylic alcohols.[3]

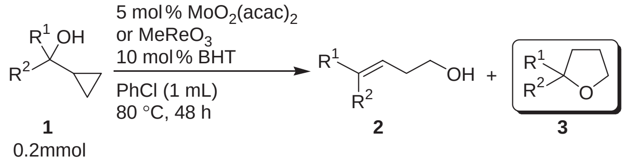

(1)

During the course of our further studies on this subject, we have now found that the use of an oxo-complex of either molybdenum[3d,4] or rhenium[5] as a catalyst for the above isomerization in place of a vanadium complex gave the corresponding 2-substituted tetrahydrofuran (**3a**) in good yield together with a slight amount of homoallylic alcohol (**2a**) (Scheme 1). We describe herein the first successful example of molybdenum- and rhenium-catalyzed isomerization of cyclopropanemethanols into the corresponding tetrahydrofurans.



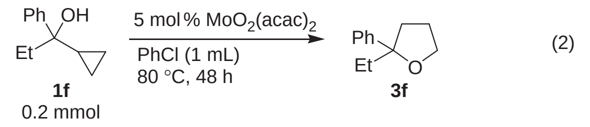
Scheme 1.

Table 1. Molybdenum- and rhenium-catalyzed isomerization of cyclopropanemethanols to tetrahydrofurans



Entry	Substrate	Catalyst	Yield of **2**/%	Yield of **3**/%[a]
1	**1a** ($R^1 = R^2 = Ph$)	$MoO_2(acac)_2$	17	82
2	**1a**	$ReMeO_3$	Tr[b]	98
3	**1b** ($R^1 = R^2 = p$-Tol)	$MoO_2(acac)_2$	12	86
4	**1b**	$ReMeO_3$	Tr	95
5[c]	**1c** ($R^1 = R^2 = 4\text{-}ClC_6H_4$)	$MoO_2(acac)_2$	51	45
6[c]	**1c**	$ReMeO_3$	49	51
7	**1d** ($R^1 = Ph$; $R^2 = H$)	$MoO_2(acac)_2$	61	0
8	**1d**	$ReMeO_3$	20	0
9	**1e** ($R^1 = Ph$; $R^2 = Me$)	$MoO_2(acac)_2$	8	88
10	**1e**	$ReMeO_3$	Tr	65
11	**1f** ($R^1 = Ph$; $R^2 = Et$)	$MoO_2(acac)_2$	Tr	91
12	**1f**	$ReMeO_3$	Tr	95
13	**1g** ($R^1 = Ph$; $R^2 = n$-Bu)	$MoO_2(acac)_2$	Tr	92
14	**1g**	$ReMeO_3$	Tr	93
15[c]	**1h** ($R^1 = Ph$; $R^2 = Bn$)	$MoO_2(acac)_2$	20	65
16[c]	**1h**	$ReMeO_3$	22	70
17	**1i** ($R^1 = R^2 = n$-Bu)	$MoO_2(acac)_2$	10	70
18	**1i**	$ReMeO_3$	Tr	68

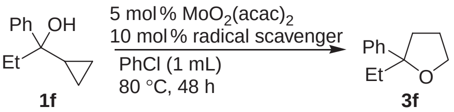
[a]Isolated yield based on **1** employed. [b]Trace. [c]For 96 h.


(2)

in the absence of inhibitor	51%
in the presence of BHT (0.02 mmol)	91%

Typical results of either molybdenum- or rhenium-catalyzed isomerization of cyclopropanemethanols to tetrahydrofurans are listed in Table 1. Similar to the case of vanadium-catalyzed isomerization of cyclopropanemethanols to homoallylic alcohols,[2] the presence of 2,6-di-*tert*-butyl-*p*-cresol (butylhydroxytoluene: BHT) as a polymerization inhibitor was essential to improve the yield of tetrahydrofurans. Thus, treatment of the cyclopropanemethanol **1f** in chlorobenzene in the presence of catalytic amounts of BHT and $MoO_2(acac)_2$ gave **3f** in an improved yield compared with the yield in the absence of BHT (Eq 2). Cyclopropanemethanol having an electron-donating methyl moiety on a phenyl ring (**1b**) was converted to **3b** in high yield (Entries 3 and 4), while treatment of the methanol having an electron-withdrawing chloro moiety on a phenyl ring (**1c**) gave **3c** in moderate yield even for a longer reaction time together with a similar yield of the homoallylic alcohol **2c** (Entries 5 and 6). The secondary alcohol **1d** was not converted to the tetrahydrofuran **3d** at all and only the homoallylic alcohol **2d**

Table 2. Effect of radical scavenger



1f 0.2 mmol → **3f**

Entry	Radical scavenger	Yield/%[a]
1	None	51
2	BHT	91
3	Galvinoxyl	55
4	*m*-Dinitrobenzene	63
5	1,1-Diphenyl-2-picrylhydrazyl	40

[a] Isolated yield based on **1d** employed.

was obtained in moderate yield (Entries 7 and 8). On the other hand, other tertiary cyclopropanemethanols like **1e**–**1h** also gave the corresponding tetrahydrofurans in good to high yields (Entries 9–16). The methanol having dialkyl substituent (**1i**) gave **3i** in good yield (Entries 17 and 18).

Next, the effect of a radical scavenger such as BHT, galvinoxyl, *m*-dinitrobenzene, and 1,1-diphenyl-2-picrylhydrazyl was investigated to obtain some information about the reaction pathway. As summarized in Table 2, the reaction was not prevented in the presence of any radical scavengers, showing that this catalytic reaction may proceed via an ionic pathway.

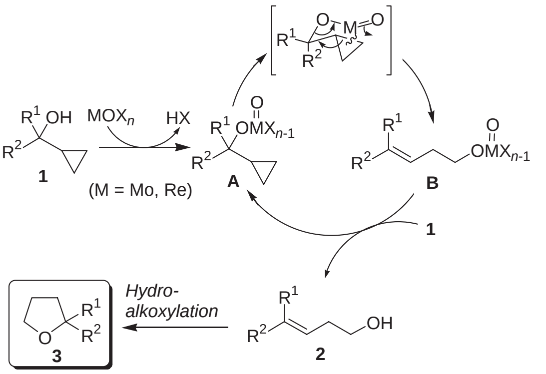
When homoallylic alcohol **2a** was heated in chlorobenzene in the presence of either $MoO_2(acac)_2$ or $ReMeO_3$ as a catalyst, **3a** was formed in 64–67% isolated yield (Eq 3). Further, when the isomerization of **1a** was carried out in the presence of a catalytic amount of K_2CO_3, **2a** was obtained as a major product together with **3a** (Eq 4). These results show that **2a** is a precursor for **3a** and also that a simple acid-catalyzed reaction might be ruled out for the formation of the product **2** from **1**.

$$\underset{0.2\ \text{mmol}}{\mathbf{2a}} \xrightarrow[\text{PhCl (1 mL)},\ 80\ {}^\circ\text{C},\ 48\ \text{h}]{5\ \text{mol\%}\ \text{MoO}_2(\text{acac})_2\ \text{or MeReO}_3,\ 10\ \text{mol\%}\ \text{BHT}} \underset{\text{Mo: 64\%, Re: 67\%}}{\mathbf{3a}} \tag{3}$$

$$\underset{0.2\ \text{mmol}}{\mathbf{1a}} \xrightarrow[\text{PhCl (1 mL)},\ 80\ {}^\circ\text{C},\ 48\ \text{h}]{5\ \text{mol\%}\ \text{MoO}_2(\text{acac})_2\ \text{or MeReO}_3,\ \mathbf{5\ mol\%\ K_2CO_3},\ 10\ \text{mol\%}\ \text{BHT}} \underset{\text{Mo: 72\%, Re: 73\%}}{\mathbf{2a}} + \underset{\text{Mo: 26\%, Re: 27\%}}{\mathbf{3a}} \tag{4}$$

A proposed catalytic cycle for the present isomerization is shown in Scheme 2: 1) an oxo metal complex reacts with cyclopropanemethanol to afford an oxo metal cyclopropanemethanolate (**A**), 2) [3,3]sigmatropic rearrangement of this alcoholate involving the C–C bond cleavage occurs to give an oxo metal homoallylic alcoholate (**B**) which reacts with another cyclopropanemethanol to give the homoallylic alcohol **2** and the oxo metal methanolate **A**, and 3) the hydroalkoxylation[6] of the initially produced homoallylic alcohol occurs intramolecularly to give the tetrahydrofuran derivative **3**.[7]

In summary, we have found a novel molybdenum- and rhenium-catalyzed isomerization of cyclopropanemethanols into tetrahydrofurans. The salient features of this catalytic behavior deserve detailed study of the ring opening reaction as well as the cyclization reaction of homoallylic alcohols.



Scheme 2.

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7 The hydroalkoxylation reaction of homoallylic alcohols might proceed via a similar pathway as proposed in Ref. 6d. However, the direct formation of **3** from the intermediate **B** could not be ruled out at the present stage.

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