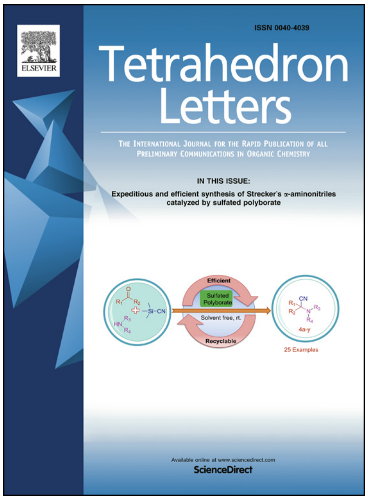

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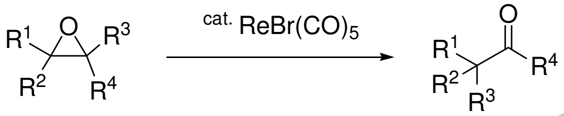

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Rhenium complex-catalyzed Meinwald rearrangement reactions of oxiranes

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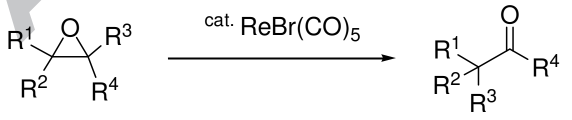
ABSTRACT

The Meinwald rearrangement reaction of oxiranes to the corresponding carbonyl compounds is efficiently catalyzed by the $ReBr(CO)_5$ complex.

Oxiranes are very important and versatile intermediates in organic synthesis, since they can be readily transformed into various functional groups. One of the useful transformations of oxiranes is the rearrangement of the oxiranes to produce carbonyl compounds (the Meinwald rearrangement); this protocol has been applied to the synthesis of various organic compounds.[1] The Meinwald rearrangement was carried out with Lewis and Brønsted acid catalysts and reagents; however, these methods have some disadvantages, such as the use of air-sensitive, corrosive or toxic catalysts and reagents or the requirement of anhydrous or inert atmosphere conditions.[2]

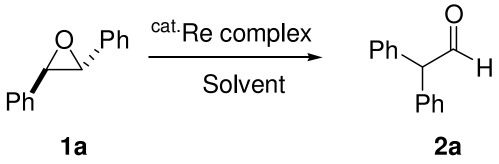
There are some reports regarding the oxo-rhenium complex–catalyzed deoxygenation of oxiranes in the presence of reducing agents giving the corresponding alkenes.[3] In contrast to the oxo-rhenium complex, we have now developed the novel catalytic ability of the rhenium complex, $ReX(CO)_5$ (X = Br and Cl), which can be used under moisture and air conditions, on the Meinwald rearrangement reaction of oxiranes to form the corresponding carbonyl compounds (Scheme 1).[4]



Scheme 1.

In order to determine the optimized reaction conditions, we investigated the effects of the rhenium complex, reaction temperature and solvent on the reaction of *trans*-2,3-diphenyloxirane (**1a**) (Table 1). When **1a** was stirred with a catalytic amount of $ReBr(CO)_5$ (5 mol%) in a 1,2-dichloroethane solvent at 80 °C for 1 h under an atmosphere of N_2, the Meinwald rearrangent of **1a** proceeded to give 1,1-diphenylacetaldehyde (**2a**) in 33% yield (Entry 1). The yield of **2a** was improved by extending the reaction times and **2a** was obtained in 94% yield at 5 h (Entries 1-3). Even when the reaction was carried out under an atmosphere of air, the Meinwald rearrangement proceeded smoothly to give **2a** in 84% yield (Entry 4). No reaction took place in the absence of the rhenium complex (Entry 5). At a lower reaction temperature (60 °C), the yield of **2a** slightly decreased (Entry 6. Even when toluene, hexane, and THF were used as the solvent, the reaction occurred to give **2a** in 50-89% yields (Entries 7-9). In the case of acetonitrile, the reaction did not proceed (Entry 10). The use of CH_2ClCH_2Cl as the solvent led to the highest yield of **2a** (Entry 3). When $ReCl(CO)_5$ was used instead of $ReBr(CO)_5$ as the catalyst, **2a** was obtained in 72% yield (Entry 11). In the case of other rhenium complexes, such as $Re_2(CO)_{10}$, and Re_2O_7, no formation of **2a** was observed (entries 12 and 13). The use of $ReCl_5$ led to a significant decrease in the yield of **2a** (Entry 14).

Table 1. Reaction of *trans*-2,3-diphenyloxirane (**1a**)[a]



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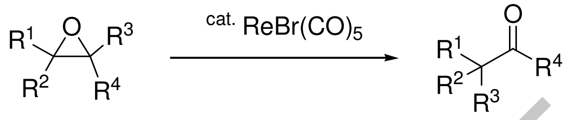
Entry	Catalyst	Solvent	Temp (ºC)	Yield (%)[b]
1[c]	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	33
2[d]	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	66
3	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	94 (72)
4[e]	$ReBr(CO)_5$	CH_2ClCH_2Cl	80	84
5	none	CH_2ClCH_2Cl	80	0
6	$ReBr(CO)_5$	CH_2ClCH_2Cl	60	52
7	$ReBr(CO)_5$	toluene	80	89
8	$ReBr(CO)_5$	C_6H_{14}	80	50
9	$ReBr(CO)_5$	THF	80	53
10	$ReBr(CO)_5$	CH_3CN	80	0
11	$ReCl(CO)_5$	CH_2ClCH_2Cl	80	72
12[f]	$Re_2(CO)_{10}$	CH_2ClCH_2Cl	80	0
13[f]	Re_2O_7	CH_2ClCH_2Cl	80	0
14	$ReCl_5$	CH_2ClCH_2Cl	80	14

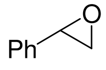
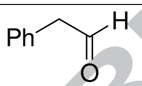
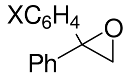
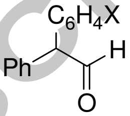
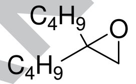
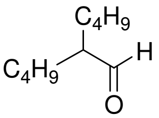
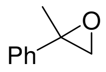
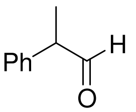
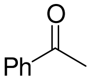
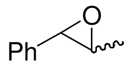
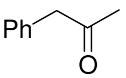
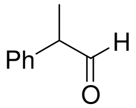
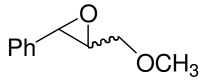
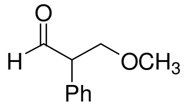
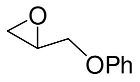
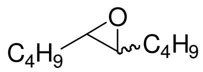
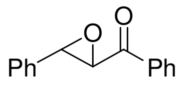
[a] Reaction conditions: **1a** (0.3 mmol), Re catalyst (5 mol%), solvent (2 mL), 5 h under an atmosphere of N_2. [b] ^{1}H-NMR yield. The number in parenthesis shows the isolated yield. [c] For 1 h. [d] For 3 h. [e] The reaction was carried out under an atmosphere of air. [f] Re catalyst (2.5 mol%).

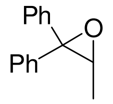
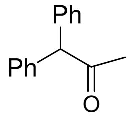
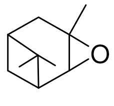
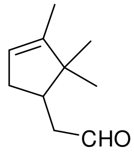
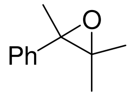
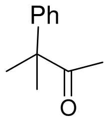
The rhenium complex is a useful catalyst for the Meinwald rearrangement reaction of oxiranes to form the corresponding carbonyl compounds.[5] These results are shown in Table 2.[6] 2-Phenyloxirane gave 2-phenylacetaldehyde, **2b**, however, the yield of **2b** was slightly decreased due to the preparation of complicated by-products (Entry 1). The Meinwald rearrangement of 2,2-diphenyloxirane selectively occurred using the rhenium catalyst to give **2a** in 93% yield (Entry 2). 2-Aryl-2-phenyl substituted oxiranes bearing electron-donating groups on the aromatic ring, such as a 2-(4-methylphenyl)- and 2-(2-methylphenyl)-3-phenyloxirane, gave 2-aryl-2-phenyl substituted acetaldehyde, **2d**, **2e**, in 89 and 81% yields, respectively (Entries 3 and 4) In the case of 2-(4-chlorophenyl)-3-phenyloxirane, in which the electron withdrawing group was substituted on the aromatic ring, 2-(4-chlorophenyl)-2-phenylacetaldehyde (**2f**) was obtained in 84% yield (entry 5). The 2,2-dialkyl substituted oxiranes, such as 2,2-dibutyloxirane, also gave 2-butylhexanal (**2g**) in 70% yield (Entry 6). On the other hand, in the case of 2-methyl-2-phenyloxirane, in which the alkyl and phenyl groups were substituted on the same carbon atom of the oxirane, 2-phenylpropanal (**2h**) was obtained with the formation of acetophenone (**2h'**) as a by-product (Entry 7). For the reaction of 2-methyl-3-phenyloxirane, 94% yield of 1-phenyl-2-pentanone (**2i**) by hydrogen migration and a small amount of **2h** (5%) by methyl migration were formed (Entry 8). Our attempt using 2-methoxymethyl-3-phenyloxirane resulted in the phenyl migrated product; 3-methoxy-2-phenylpropanal (**2j**), as the main product (Entry 9).[7] However, in the case of 2-phenoxymethyloxirane, the Meinwald rearrangement did not occur (Entry 10). For the reaction of 2,3-dialkyl and electron-withdrawing group substituted oxiranes, starting materials were recovered (Entries 11 and 12). The Meinwald rearrangement of tri-substituted oxirane, 2-methyl-3,3-diphenyloxirane, proceeded selectively to give the corresponding carbonyl compound **2n** in 99% yield (Entry 13). The rhenium-catalyzed reaction of tri-substituted cyclic oxirane, α-pinene oxide, gave the skeletal rearrangement product **2o** in low yield (Entry 14).[2In: (a),8] In the case of tetra-substituted oxirane, such as 2,2,3-trimethyl-3-phenyloxirane, 3-phenyl-3-methyl-2-butanone (**2p**) was formed in 96% yield via the migration of phenyl group (Entry 15).

Table 2. Reaction of various oxiranes[a]



1 **2**

Entry	Oxirane	Product	Yield (%)[b]
1	 (**1b**)		73 (**2b**)
2	 X = H (**1c**)		93 (**2a**)
3	X = 4-CH_3 (**1d**)		89 (**2d**)
4	X = 2-CH_3 (**1e**)		81 (**2e**)
5	X = 4-Cl (**1f**)		84 (**2f**)
6	 (**1g**)		70 (**2g**)
7	 (**1h**)		45 (**2h**)
			18 (**2h'**)
8	 (**1i**)		94 (**2i**)
			5 (**2h**)
9	 (**1j**)		81 (**2j**)
10	 (**1k**)		0 (**2k**)
11	 (**1l**)		0 (**2l**)
12			0 (**2m**)

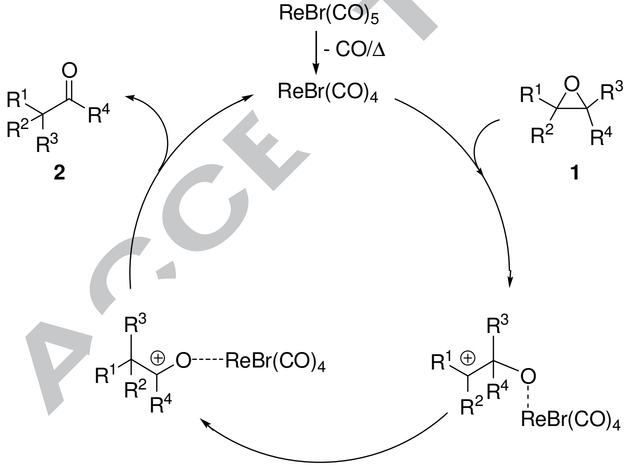
	(**1m**)		
13	 (**1n**)		99 (**2n**)
14	 (**1o**)		26 (**2o**)[c]
15	 (**1p**)		96 (**2p**)

[a] Reaction conditions: oxirane (0.3 mmol), $\mathrm{ReBr(CO)_5}$ (5 mol%), $\mathrm{CH_2ClCH_2Cl}$ (2 mL), at 80 ℃ for 1 h under an atmosphere of $\mathrm{N_2}$.

[b] Isolated yield.

[c] ^{1}H NMR yield.

Based on these observations, the plausible reaction pathway for the rhenium-catalyzed Meinwald rearrangement reaction of oxiranes is shown in Scheme 2. First, the decarbonylation of $\mathrm{ReBr(CO)_5}$ to form $\mathrm{ReBr(CO)_4}$, which is the coordinative unsaturated 16-electron complex, is the first step of the catalytic reaction.[9] The coordination of rhenium species to the oxygen atom of oxirane followed by the C-O bond cleavage of the oxirane generates the stable carbocation.[10] The hydrogen migration from the carbocation smoothly proceeded to give the corresponding carbonyl compound. On the other hand, when phenyl is at the β-position of the carbocation, the phenyl group will preferentially migrate through the well-established phenonium ion to form the corresponding aldehyde.



Scheme 2. A plausible reaction pathway

We showed that the rhenium complex catalyzed the Meinwald rearrangement reaction of oxiranes to the corresponding carbonyl compounds. The application of the reaction and determining the reaction pathway are now in progress.

Acknowledgments

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References and notes

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5) Hua et al. reported the $ReBr(CO)_5$-catalyzed synthesis of cyclic carbonates by the reaction of oxiranes with carbon dioxide. In the manuscript, they indicated that the rhenium complex showed a good catalytic ability for only the oxiranes derived from the terminal alkenes. See: Jiang, J.-L.; Gao, F.; Hua, R.; Qiu, X. *J. Org. Chem.* **2005**, *70*, 381-383.

6) General procedure: A 1,2-dichloroethane (2 mL) solution of oxirane (0.3 mmol) and $ReBr(CO)_5$ (5 mol%) was stirred under an atmosphere of nitrogen at 80 ^{o}C for 1-5 h. After the reaction was complete, H_2O was added to the reaction mixture and extracted with ethyl acetate. 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 the carbonyl compounds. Further purification was carried out by recyclable preparative HPLC, if necessary. Yields were determined by ^{1}H-NMR using internal standard.

7) The $AuCl_3/AgSBF_6$-catalyzed rearrangement of **1j** also formed **2j** as by-product. See Ref . 2Au: (a).

8) We could not isolate the compound **2o**, due to the decomposition of **2o** during the purification.

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10) We have shown that C-O bond of ethers was effectively cleavaged by rhenium complex. See Ref. 4g and 4l.

Supplementary Material

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

Highlights

A new catalytic ability of rhenium complex is described.
A new method of the Meinwald rearrangement reaction is developed.
A scope and limitation of the rhenium catalytic system is disclosed.