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Stereospecific Deoxygenation of Aliphatic Epoxides to Alkenes under Rhenium Catalysis

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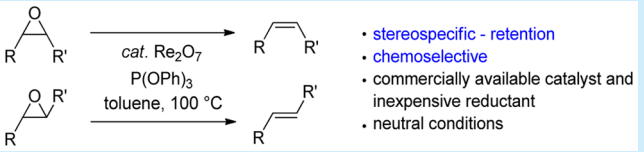
Supporting Information

ABSTRACT: The combination of a catalytic amount of Re_2O_7 and triphenyl phosphite as a reductant is effective for the deoxygenation of unactivated aliphatic epoxides to alkenes. The reaction proceeds stereospecifically with variously substituted epoxides under neutral conditions and is compatible with various functional groups. Protection and deprotection of a double bond functionality using an epoxide are shown as an example of the current rhenium-catalyzed deoxygenation protocol. The effect of reductants for the stereoselectivity has also been studied, indicating that the use of electron-deficient phosphines or phosphites is the key for the stereospecific deoxygenation.



Deoxygenation of epoxides into alkenes is a fundamental but important transformation in both organic[1] and biological chemistry.[2] Although the corresponding reverse oxygenation reactions, epoxidation of alkenes, have been well-investigated and widely applied in organic synthesis,[3] catalytic deoxygenation of epoxides leading to alkenes has been much less developed. Stemming from the seminal work by Sharpless et al. in 1972 using a stoichiometric amount of WCl_6 and ^{n}BuLi, a variety of promoters have been developed for the effective deoxygenation of epoxides.[4,5] In recent years, catalytic deoxygenation has been realized with high valent oxorhenium complexes including $MeReO_3$ and $ReIO_2(PPh_3)_2$, and an oxoruthenium complex together with PPh_3, H_2, or Na_2SO_3 as reductants.[6] While synthetically attractive, most of these protocols still suffer from relatively high catalyst loadings, harsh conditions, and limited scope of substrates (e.g., only effective for activated epoxides such as styrene oxides (aryl epoxides) or conformationally locked cyclohexene oxides (cyclic epoxides)). Far less attention has been focused on *stereospecific deoxygenation of unactivated aliphatic epoxides*. This is because the reported catalytic system generally requires high temperatures (usually 150 °C or higher) and longer reaction times (12−100 h), which tend to form side products from isomerization of intermediates. The reaction also occurs without control of product stereochemistry, leading to the formation of the thermodynamically favored (*E*)-alkene as the major product.[6] Thus, the operationally simple and stereospecific deoxygenation of the more abundant unactivated epoxides with a combination of an inexpensive catalyst and reductant under mild conditions would be of significant interest.

Based on our recent studies on the use of rhenium complexes as valuable catalysts for organic reactions,[7] we initiated a project studying the chemo- and stereoselective deoxygenation of epoxides with readily available catalysts and practical reductants under mild reaction conditions. We now report the rhenium-catalyzed deoxygenation of epoxides to alkenes under relatively mild conditions using triphenyl phosphite as a reductant.[8] In addition, we disclose here that the structure of the reductants affects the regioselectivity of the deoxygenation.

Deoxygenation of *cis*-1,6-diphenyl-3-hexene oxide **1a** was carried out as a model reaction in toluene at 100 °C in the presence of various rhenium catalysts (10 mol %−Re) with PPh_3 as a reductant. Although the reaction took place in the presence of $MeReO_3$, $ReOCl_3(PPh_3)_2$, and $ReIO_2(PPh_3)_2$, which showed high catalytic performance against styrene oxides and cyclohexene oxide under the previously reported reaction conditions,[6] moderate to low stereoselectivities were observed (Table 1, entries 1−3). Low-valent rhenium complexes including $Re_2(CO)_{10}$ and $[ReBr(CO)_3(thf)]_2$ were ineffective, and **1a** was recovered intact. Among the catalysts screened, Re_2O_7, which is less expensive and easy to handle, showed the highest catalytic efficiency to yield **2a** in >99% yield (*Z*/*E* = 60/40) and thus was chosen as the catalyst for further optimization (entry 4).[9,10] Excellent stereoselectivity (*Z*/*E* = 92/8) was observed using $P(OPh)_3$ as a reductant in place of PPh_3 (entry 5). It should be noted that $P(OPh)_3$ is a valuable reductant due to its low cost, low toxicity, and good stability in the air.[11] Finally, **1a** was isolated in 94% yield (>99% GLC yield) with excellent stereocontrol even with a reduced catalyst loading (2.5 mol %) (entry 6). Control experiments demonstrated that no deoxygenation by $P(OPh)_3$ occurred in the absence of

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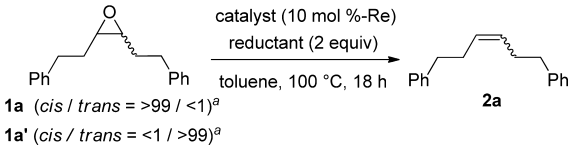
Table 1. Rhenium-Catalyzed Deoxygenation of Epoxide 1a



1a (*cis* / *trans* = >99 / <1)[a]

1a' (*cis* / *trans* = <1 / >99)[a]

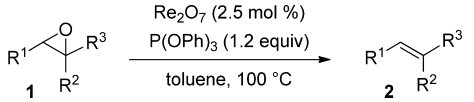
entry	epoxide	catalyst	reductant	yield[b]/%	*Z*/*E*[a]
1	**1a**	$MeReO_3$	PPh_3	97	88/12
2	**1a**	$ReOCl_3(PPh_3)_2$	PPh_3	59	24/76
3	**1a**	$ReIO_2(PPh_3)_2$	PPh_3	87	65/35
4	**1a**	Re_2O_7	PPh_3	>99	60/40
5	**1a**	Re_2O_7	$P(OPh)_3$	>99	92/8
6[c]	**1a**	Re_2O_7	$P(OPh)_3$	>99 (94)	97/3
7[d]	**1a**	Re_2O_7	$P(OPh)_3$	>99	98/2
8[e]	**1a**	Re_2O_7	$P(OPh)_3$	>99	99/1
9[c]	**1a'**	Re_2O_7	$P(OPh)_3$	>99 (96)	1/99
10[e,f]	**1a**	Re_2O_7	$P(OPh)_3$	>99 (92)	98/2

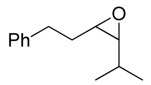
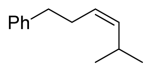
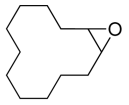
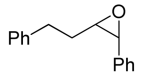
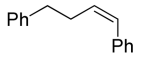
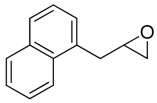
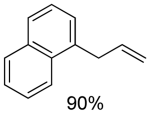
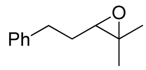
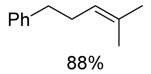
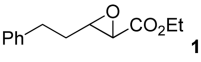
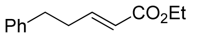
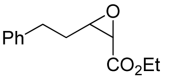
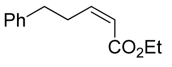
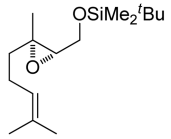
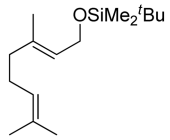
[a]Determined by GLC. [b]Determined by ^1H NMR. Values in parentheses are isolated yields. [c]2.5 mol % of Re_2O_7 and 1.2 equiv of $P(OPh)_3$ for 6 h. [d]2.5 mol % of Re_2O_7 and 1.2 equiv of $P(OPh)_3$ at 80 °C for 36 h. [e]0.25 mol % of Re_2O_7 and 1.2 equiv of $P(OPh)_3$ for 48 h. [f]5 mmol scale.

Re_2O_7 even at 150 °C for 24 h. Importantly, almost complete retention of stereochemistry (*Z*/*E* = 98/2) was observed when the reaction was examined at 80 °C, although a prolonged reaction time (36 h) was required for achieving complete conversion of **1a** (entry 7). Moreover, deoxygenation occurred with complete retention of stereochemistry to furnish **2a** quantitatively, when the amount of catalyst loading was decreased to 0.25 mol % (entry 8). Under the same reaction conditions described in entry 6, *trans*-1,6-diphenyl-3-hexene oxide **1a'** furnished exclusively the *E*-olefin in 96% yield with complete retention of configuration (*Z*/*E* = 1/99) (entry 9). A similar reaction time was required for complete conversion of these *cis*- and *trans*-epoxides. The results in entries 6 and 9 clearly showed that the current deoxygenation proceeded stereospecifically. The reaction proceeded even on a gram scale. Treatment of a mixture of 1.26 g (5.0 mmol, *cis*/*trans* = >99/<1) of **1a** with a Re_2O_7 catalyst (1.0 mol %) in toluene in a 50 mL Schlenk flask at 100 °C for 18 h gave 1.09 g of **2a** with retention of stereochemistry (entry 10).

With the optimized reaction conditions in hand, a variety of epoxides were subjected to the deoxygenation reaction in the presence of Re_2O_7. The series of epoxides having linear, branched, and cyclic alkyl chains shown in Table 2 were deoxygenated to the corresponding alkenes with complete retention of stereochemistry in all cases (all the reactions were examined on 0.50 mmol scale). For example, isopropyl group substituted epoxide **1b** and cyclic *cis*-cyclododecene oxide **1c** were deoxygenated efficiently to give the corresponding olefins **2b** and **2c** with complete retention of stereochemistry (entries 1 and 2). The deoxygenation of arylene oxide **1d** proceeded with high selectivity (entry 3). To determine the influence of the number of substituents on the epoxide rings, deoxygenations of mono- and trisubstituted aliphatic epoxides **1e** and **1f** were carried out next. The epoxides gave the corresponding mono- and trisubstituted olefins **2e** and **2f** in excellent yields even with a reduced amount of catalyst (entries 4 and 5). The current protocol was also extended to catalytic deoxygenation of *α*,*β*-epoxyesters. Both (*E*)- and (*Z*)-*α*,*β*-unsaturated esters **2g** and **2h** were obtained selectively in 93% and 90% yields from

Table 2. Rhenium-Catalyzed Deoxygenation of Epoxides 1[a]



entry	epoxide	time / h	alkene
1	 (*cis* / *trans* = >99 / <1) **1b**	6	 91% (*Z* / *E* = 98 / 2) **2b**
2	 (*cis* / *trans* = 98 / 2) **1c**	8	 74% (*Z* / *E* = 98 / 2) **2c**
3[b]	 (*cis* / *trans* = 95 / 5) **1d**	2	 91% (*Z* / *E* = 93 / 7) **2d**
4	 **1e**	8	 90% **2e**
5[b]	 **1f**	48	 88% **2f**
6	 (*cis* / *trans* = <1 / >99) **1g**	6	 93% (*Z* / *E* = <1 / >99) **2g**
7	 (*cis* / *trans* = 97 / 3) **1h**	6	 90% (*Z* / *E* = 94 / 6) **2h**
8[b]	 **3**	48	 81% (*Z* / *E* = <1 / >99) **4**

[a]0.50 mmol scale. Ratio of stereoisomers was determined by GLC. [b]1.0 mol % of Re_2O_7 was used.

trans- and *cis*-*α*,*β*-epoxyesters **1g** and **1h** with excellent stereocontrol (entries 6 and 7).

Since the reaction proceeded under neutral and relatively mild conditions, chemoselective deoxygenation was achieved in the presence of other chemicals including ketone, ester, ether, halide, and nitrile (Table S1 in Supporting Information).[12] The reaction proceeded without affecting these functional groups to furnish the corresponding olefin **2a** in >93% yields with almost complete retention of stereochemistry, and additives were recovered quantitatively. When aldehyde, 3-phenylpropanal, was added to the reaction mixture, the recovery yields of the additive was decreased to 48%.

The excellent tolerance of functional groups demonstrated above makes the current reaction quite useful especially for the total synthesis of natural products. This is further demonstrated by the stereospecific deoxygenation of the monoterpene oxide, geraniol oxide (Table 2, entry 8). Deoxygenation of the hydroxy group protected geraniol oxide **3** proceeded without isomerization of the double bond to afford **4** in 81% yield. This result illustrates good chemoselectivity against the silyl group as

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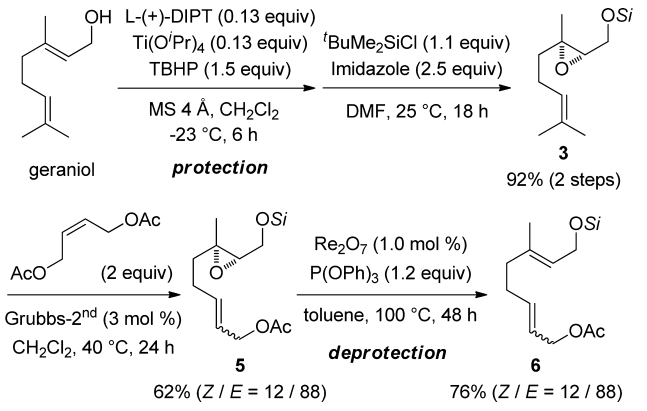
well as the wide substrate scope of the current stereospecific deoxygenation even with the sterically crowded trisubstituted epoxide. Furthermore, it is possible to *protect* the double bond functionality by applying the current rhenium-catalyzed deoxygenation.[1] For example, olefin cross-metathesis[13] following the deoxygenation (deprotection) of **3**, which was prepared by the epoxidation (protection) of geraniol, resulted in the selective functionalization of one of the double bonds with the allylic double bonds intact (Scheme 1). In contrast, the direct olefin metathesis of **4** or geraniol without the current *protection/deprotection* protocol gave a complex mixture of products.

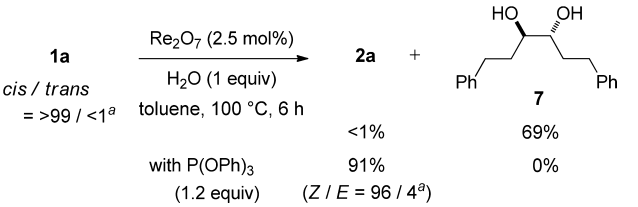
Scheme 1. Chemoselective Transformation of Double Bond by Epoxidation/Deoxygenation Protocol (*Si* = $SiMe_2{}^tBu$)



As shown in Table 1, the choice of reductants is crucial for the current stereospecific deoxygenation of epoxides. Preliminary studies to elucidate the origin of the selectivity and the reaction mechanism were carried out. First, the deoxygenation of **1a** in the presence of several phosphines and phosphites was carried out.[14] Among the results obtained, we focused on the following two observations. (1) The deoxygenation occurred efficiently when triarylphosphines or phosphites were used as reductants. Alkylphosphines including tributylphosphine, tricyclohexylphosphine, and 1,2-bis(diphenylphosphino)ethane did not promote the reaction. (2) Good to excellent stereoselectivities were observed with the sterically hindered or electron-deficient phosphines and phosphites. Control experiments, in which (*Z*)-**2a** was subjected independently to the reaction conditions, demonstrated that none of the stereoisomer (*E*)-**2a** was produced in the presence of Re_2O_7 and phosphines and phosphites. This result clearly indicates that the isomerization from the (*Z*)- to (*E*)-isomer occurred during the deoxygenation process.

To obtain insight into the effect of phosphite, the reaction of Re_2O_7 with an equimolar amount of $P(OPh)_3$ in C_6D_6 was monitored by ^{31}P NMR spectroscopy. The formation of $O{=}P(OPh)_3$ was observed even at 25 °C for 5 min, indicating that the current catalytic reaction is initiated by the rapid deoxygenation of Re_2O_7 by $P(OPh)_3$ to generate the active catalytic species. Furthermore, $P(OPh)_3$ was found to dramatically change the reactivity of Re_2O_7 by the reduction of a rhenium center. In the presence of 1.2 equiv of $P(OPh)_3$, the expected **2a** was obtained in 91% yield with high stereoselectivity (*Z*/*E* = 96/4) even in the presence of water (Scheme 2). This result also proved the robustness of the present stereoselective deoxygenation reaction against water. In

Scheme 2. Reactivity Switch of Re_2O_7 in the Presence of $P(OPh)_3$



[a]Determined by GLC.

sharp contrast, the yield of olefin **2a** decreased less than 1% and the formation of 1,2-diol **7** was observed in 69% yield, when the same reaction was examined in the absence of $P(OPh)_3$.[15] We further confirmed that treatment of 0.50 equiv of $P(OPh)_3$ with 2.5 mol % of Re_2O_7 and **1a** for 6 h furnished a 50% yield of **2a** with high stereoselectivity (*Z*/*E* = 96/4). These results imply that phosphite plays a role in (1) the reduction of the high valent Re_2O_7 to form the rhenium active species suitable for the achievement of stereospecific deoxygenation of epoxides and (2) the regeneration of the rhenium species by deoxygenation after one catalytic cycle.

Based on the above observations, a plausible reaction mechanism is shown in Figure 1.[16] The reaction initiates with

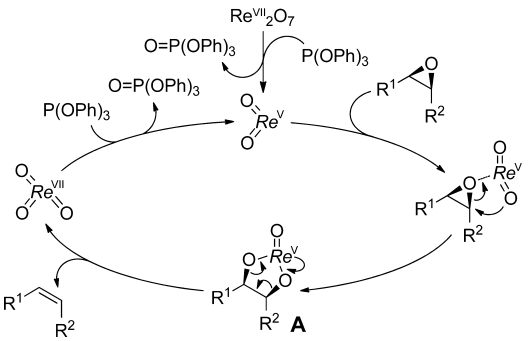


Figure 1. Proposed reaction mechanism.

the rapid reduction of Re_2O_7 by $P(OPh)_3$.[17] Subsequent coordination of the epoxide to the resulting oxorhenium species followed by the ring-opening of the epoxide gives five-membered-ring rhena-2,5-dioxolane intermediate **A** with retention of configuration. Finally, olefin extrusion via the cleavage of **A** and regeneration of the oxorhenium species by reduction with $P(OPh)_3$ complete the catalytic cycle.[18]

In summary, the present study describes the operationally simple deoxygenation of unactivated aliphatic epoxides to the corresponding alkenes using the reductant, $P(OPh)_3$, with Re_2O_7 catalyst. The reductant and catalyst are both inexpensive. The reaction proceeded with complete regioselectivity with broad functional group tolerance. This catalytic system promises to be useful, especially in natural products and pharmaceutical syntheses, which require mild conditions, selectivity, and functional group tolerance.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic data for all new compounds, and copies of ^1H and ^{13}C NMR spectra. The

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Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01583.

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Notes

The authors declare no competing financial interest.

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(10) Investigation of solvents with 2.5 mol% of Re_2O_7 and 1.2 equiv of $P(OPh)_3$ for 6 h: ClC_6H_5 >99% (*Z*/*E* = 97/3), decane >99% (97/3), $ClCH_2CH_2Cl$ >99% (97/3), dioxane >99% (97/3), MeCN 22% (95/5), DMF 18% (82/18).

(11) The price *per* 500 g of $P(OPh)_3$ is $26, and that for PPh_3 is $82 (TCI America Fine Chemicals).

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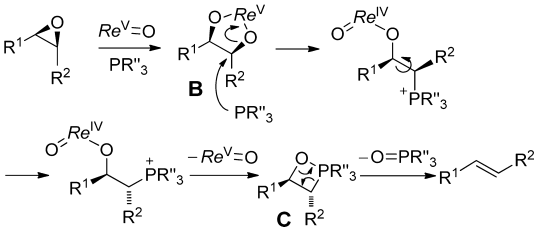
(14) Effect of phosphines and phosphites (1.2 equiv) on the regioselectivity in the deoxygenation of **1a** with 2.5 mol% of Re_2O_7 for 6 h: PPh_3 >99% (*Z*/*E* = 60/40), P(furyl)$_3$ 76% (68/32), P(*o*-tol) 7% (98/2), $P(C_6F_5)_3$ 55% (95/5), $P(O(4\text{-}FC_6H_4))_3$ >99% (97/3), P^nBu_3 2%, PCy_3 0%, dppe 7%.

(15) Diol **7** was not converted to olefin **2a** in the presence of a Re_2O_7 catalyst with $P(OPh)_3$. Therefore, the active catalytic species generated from the reduction of Re_2O_7 with $P(OPh)_3$ should directly convert **1a** to **2a** without producing **7**, thus having different reactivity compared with the original high valent Re_2O_7 species.

(16) For a mechanism study of rhenium-catalyzed deoxygenation of epoxides, see: Bi, S.; Wang, J.; Liu, L.; Li, P.; Lin, Z. *Organometallics* **2012**, *31*, 6139.

(17) Because the regioselectivity of the reaction depends on the choice of reductants as noted in ref 14, coordination of phosphite to oxorhenium species cannot be ruled out.

(18) The decrease of the selectivity in the reaction using PPh_3 as a reductant (Table 1, entry 4) might be explained by considering the intermolecular nucleophilic attack of PPh_3 on the carbon atom of rhena-2,5-dioxolane intermediate **B** followed by PPh_3-facilitated reductive deoxygenation *via* the oxaphosphetane intermediate **C**.



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