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Isomerization of allylic silyl ethers catalyzed by $ReO_3(OSiR_3)$ complexes

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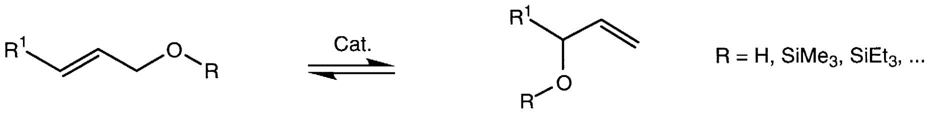
Abstract

Efficient isomerization of allylic alcohols and allylic ethers at room temperature by rhenium (VII) oxo complexes is described.

Keywords: rhenium; catalysis; rearrangements; isomerization.

The 1,3-transposition of a hydroxy group on an allyl moiety using a metal oxo catalyst is an important transformation in organic synthesis. The isomerization of allyl alcohols can be catalyzed at high temperatures (ca. 130–200°C) by complexes such as $VO(OR)_3$ or $WO(OR)_4$, or at room temperature by $VO(acac)_2$ or $MoO_2(acac)_2$ when activated by $Me_3SiOOSiMe_3$ or MoO_2X_2 (X=Cl, O^tBu).[1–3] Recently, we have reported rhenium(VII) catalysts that are very active at room temperature or below for this process.[4] The use of these catalysts leads to an equilibrium between the substrate and the product. We would like to determine whether the isomerization of alcohols can be extended to other substrates and whether this equilibrium is then modified. Therefore, we decided to apply the isomerization reaction to allyl silyl ethers. We report here some reaction studies using the trioxorhenium complexes $ReO_3(OSiR_3)$ (R=Me, Ph)[5,6] as catalysts and the trialkylsilyl allylic ethers as substrates (Scheme 1).

Wilkinson et al. reported that $ReO_3(OSiMe_3)$ can react with the protected alcohol $ROSiMe_3$ (R=Me or R=^tBu) to give the corresponding complex $ReO_3(OR)$ in good yield.[7] We found that this reaction can be applied to the catalytic isomerization of trialkylsilyl allyl ethers. For example, using $ReO_3(OSiMe_3)$ as a catalyst in dichloromethane at 25°C, 100 equivalents of *trans*-1-(trimethylsiloxy)hex-2-ene were



Scheme 1.

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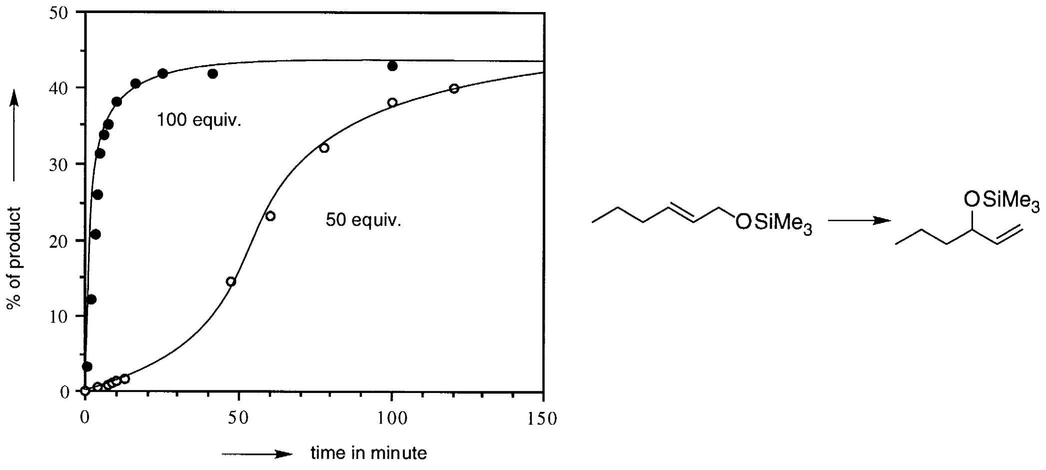
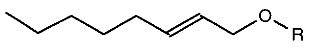
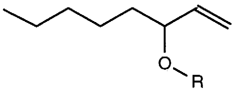
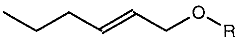
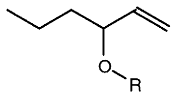
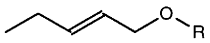
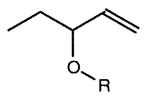
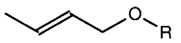
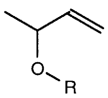
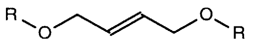
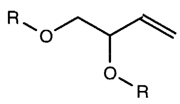


Fig. 1. Conversion of *trans*-1-(trimethylsiloxy)hex-2-ene into 3-(trimethylsiloxy)hex-1-ene in CH_2Cl_2 at 25°C, $[ReO_3(OSiMe_3)]=4.4\times10^{-3}$ M, 100 and 50 equivalents of substrate

Table 1
Equilibrium of different allylic substrates in CH_2Cl_2 at room temperature, catalyst: $ReO_3(OSiMe_3)$

Entry	Equilibrium			R	Ratio a : b
	a		b		
1		$\rightleftharpoons$		H	35 : 65
				$SiMe_3$	53 : 47
2		$\rightleftharpoons$		H	40 : 60
				$SiMe_3$	55 : 45
				$SiEt_3$	62 : 38
				Si^tBuMe_2	57 : 43
3		$\rightleftharpoons$		H	27 : 73
				$SiMe_3$	41 : 59
4		$\rightleftharpoons$		H	26 : 74
				$SiMe_3$	42 : 58
5		$\rightleftharpoons$		H	26 : 74
				$SiMe_3$	42 : 58

isomerized at an initial rate of 8 turnovers per minute, reaching equilibrium in less than 60 minutes (Fig. 1). If a coordinating solvent like acetonitrile or THF was used, the rate of the reaction was reduced (respectively, 0.8 and 0.4 maximum turnovers per minute vs 8 in CH_2Cl_2). When only 50 equivalents of the substrate were used, we observed an initiation period at the beginning of the reaction, and approximately 2.5 hours were required to reach equilibrium. The analogous triphenylsiloxy derivative $ReO_3(OSiPh_3)$ or rhenium oxide Re_2O_7 also catalyzed the reaction. With $ReO_3(OSiPh_3)$ and 100 equivalents of substrate, a small induction period was needed and a maximum rate of 3.5 turnovers per minute was measured. With Re_2O_7, and in the same conditions, the rate of the reaction could not be quantified because Re_2O_7 is not soluble in dichloromethane.

Table 1 shows the result of the isomerization of different substrates in dichloromethane at room temperature with $ReO_3(OSiMe_3)$ as catalyst. In each case, when the alcohol was replaced by the trimethylsiloxy group, the proportion of primary allylic ether increased by about 15% at equilibrium. For instance, the equilibrium with hexenol as substrate was composed of 40% of the primary alcohol (hex-2-en-1-ol) and 60% of the secondary alcohol (hex-1-en-3-ol) (entry 2). If the hydroxy was replaced by a trimethylsiloxy group, the ratio was inverted (55% of the primary ether and 45% of the secondary ether).

The equilibrium between the two isomers could be displaced by simply varying the substituents on the silicon. When the triethylsiloxy group was used, the ratio between the primary and the secondary hexenyl ethers was 62:38, but the catalytic process was very slow (with 100 equivalents of substrate, several hours were required to reach equilibrium) (entry 2). Curiously, with the *tert*-butyldimethylsiloxy group the ratio was not improved (57% of the primary ether and 43% of the secondary ether).

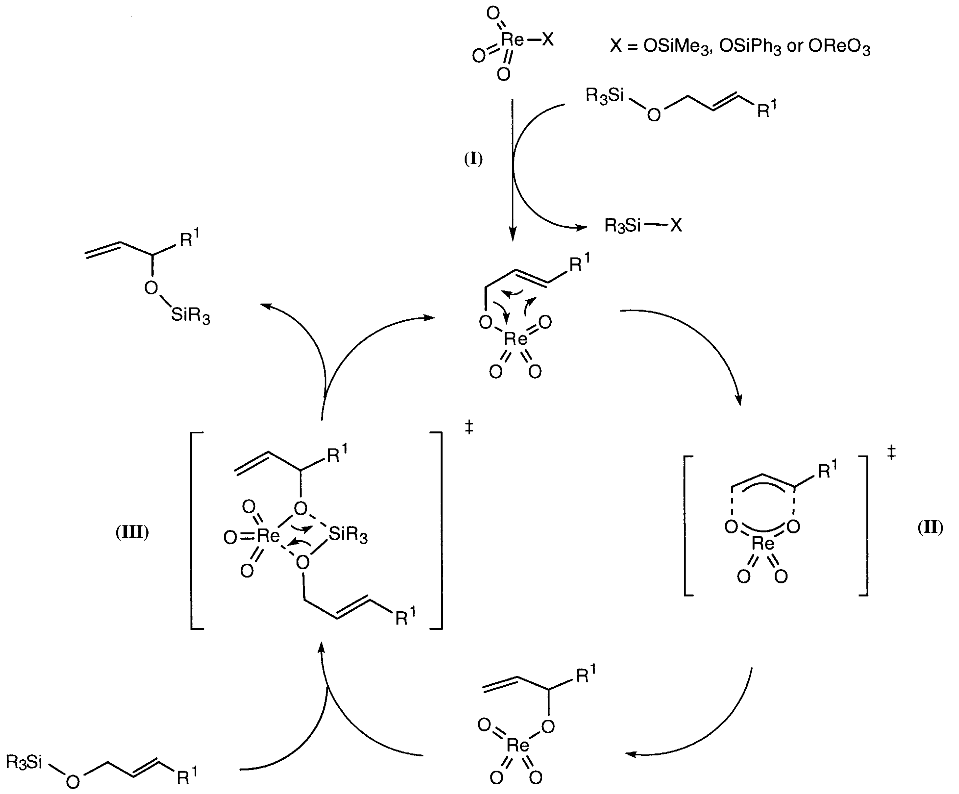


Fig. 2. Proposed mechanism of the rhenium-catalyzed isomerization of allyl silyl ethers

We propose a mechanism for the isomerization process which is inspired by the one by Chabardes et al.[1,8] The first step is an exchange of the trialkylsiloxy ligand or tetraoxorhenium unit of the precursor with the substrate to form the active species (Fig. 2, step I).[9,10] A migration of the allyl group to a metal oxo unit then takes place (step II). The product is obtained after an exchange step with the substrate (step III). The low reaction rate in coordinating solvents (vide supra) could be explained by the competition for coordination of the Lewis-acidic rhenium center between the substrate and the solvent in step III. Furthermore, the exchange between $ReO_3(OSiMe_3)$ and $ROSiMe_3$ has recently been evidenced by ^{17}O NMR studies.[11]

In conclusion, we have shown that the reactivity of a silylated alcohol toward a high oxidation state transition metal can be applied towards an efficient catalytic isomerization process. This process may be applied in the future to other kinds of allyl ethers, and to organic synthesis in general.

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