Allylic Alcohol Isomerization and Mechanistic Considerations with CH_3ReO_3

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Summary: A mechanism for the isomerization of allylic alcohols by CH_3ReO_3 has been constructed on the basis of ^{18}O isotopic studies and involves exchange between the alcohol and metal-bonded O atoms, in contrast to a previously published mechanism, which involved the 1,3-transposition of the O atom on the alcohol. Our method of analysis does not directly rule out this latter mechanism.

1. Introduction

A study detailed in this journal using CH_3ReO_3 had suggested that the mechanism of allylic alcohol isomerization was based upon a 1,3-transposition of the O atoms in the allylic alcohol and did not involve O atom exchange between the metal-bonded O atoms and that on the alcohol.[1] The isomerization of allyl alcohols is useful, as it represents a Claisen-type rearrangement[2] and is important for both fundamental[3] and practical reasons.[4] Interestingly, earlier in a study conducted using $ReO_3(OSiR_3)$, a mechanism involving O atom exchange was proposed.[5] On the basis of the results of our recently communicated work on the syntheses and structures of the complexes $MoCl_2(O)(O_2)(OPR_3)_2$ (OPR_3 = $OPCH_3Ph_2$, $OPPh_3$) and their potential use as isomerization catalysts for some allylic alcohols,[6] we had evidence that O atom exchange was at work with our Mo systems. This paper details the use of CH_3ReO_3 as an isomerization catalyst and list the data we obtained on the basis of GC-MS analyses. Our results suggest that the mechanism of isomerization of the allylic alcohol includes O atom exchange between the metal-bonded O atoms and the O atom on the alcohol.

Experimental Section

2.1. General Data. A Shimadzu QP5050A GCMS instrument was used for the mass spectra determinations and isotopic studies. Solvents were either used as received from commercial suppliers or dried and distilled under nitrogen if necessary. Chloroform was dried over calcium hydride. Benzene was dried over sodium benzophenone ketyl. The allylic alcohols used in this study were obtained from commercial sources or synthesized according to the literature.[7] Purities were assessed by ^1H NMR (recorded on a Varian XL-400 spectrometer) and GC-MS. Some operations were carried out using standard Schlenk techniques. Some isomerization investigations were done in chloroform-*d* with 10 mM catalyst concentrations and 150 mM allylic alcohols at room temperature. The compound CH_3ReO_3 was obtained from Strem and Aldrich Chemicals and melted sharply at the literature value of 111 °C. The ^1H NMR spectrum of this CH_3ReO_3 contained only one resonance. This commercial compound thus appeared to be pure. As a further precaution, we used, in some determinations, CH_3ReO_3, which was purified by sublimation. We found no difference in reactivity in the compound used after sublimation compared to that used as obtained. The compounds 10% and 97% ^{18}O H_2O were purchased from Icon Isotopes and Sigma Chemical Co., respectively. Mass spectra were calculated using the program Mass Spec Calculator Professional, Version 4.06.

2.2. GC-MS Quantitative Analysis. Geraniol with CH_3ReO_3. An 80 mg portion of geraniol (0.52 mmol), 80 mg of cyclooctane (internal standard), and 10 mol % (0.052 mmol) of CH_3ReO_3 as catalyst were dissolved in 2 mL of dry C_6H_6. The reaction was performed under moisture-free conditions and was stirred under an N_2 atmosphere for 3 days. The course of reaction was monitored by GC-MS every 12 h and the concentrations from the conversion of geraniol to linalool calculated from standard calibration curves ($r^2 = 0.99$, for each chemical) recorded before the reaction.

Preparation of ^{18}O-Enriched 2-Phenyl-3-buten-2-ol. This material was prepared according to the literature procedure,[7] except for the use of ^{18}O-enriched acetophenone. The compound was obtained in reasonably pure form by vacuum distillation at 73−74 °C (1 mmHg). MS data confirmed the presence of ^{18}O atoms in the alcohol (*m*/*z* 150).

Reactions between ^{18}O-Enriched 2-Phenyl-3-buten-2-ol and CH_3ReO_3. Stoichiometric Run. This reaction was conducted by placing 11.96 mg (0.08 mmol) of 7.6% ^{18}O-enriched alcohol into a vial and adding 0.7 mL of dry C_6H_6. CH_3ReO_3 (20.0 mg, 0.08 mmol) was then added. This mixture was allowed to stand for approximately 4 days and was monitored by GC-MS.

Catalytic Run. This reaction was conducted by placing 22.5 mg (0.15 mmol) of enriched alcohol and 22.5 mg of di-*n*-butyl ether into a moisture-free reaction flask and adding 3.0 mL of dry C_6H_6. CH_3ReO_3 (3.8 mg, 0.015 mmol) was then added. This was allowed to stand under an N_2 atmosphere for approximately 4 days and was monitored by GC-MS.

Acid Catalysis: Reactions between 2-Phenyl-3-buten-2-ol and Hydrochloric Acid (or Perchloric Acid). Stoichiometric Run. A 4.4 mg portion of 2-phenyl-3-buten-2-ol (0.03 mmol) in 1.5 mL of $CHCl_3$ and 6 μL of 5 M HCl or 15 μL of 2 M $HClO_4$ (0.03 mmol) were stirred at room temperature for 3 days and the reaction monitored by GC-MS periodically over the reaction period.

Catalytic Run. A 0.44 g portion of 2-phenyl-3-buten-2-ol (3 mmol) in 5 mL of $CHCl_3$ and 15 μL of 2 M $HClO_4$ (10 mol

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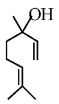
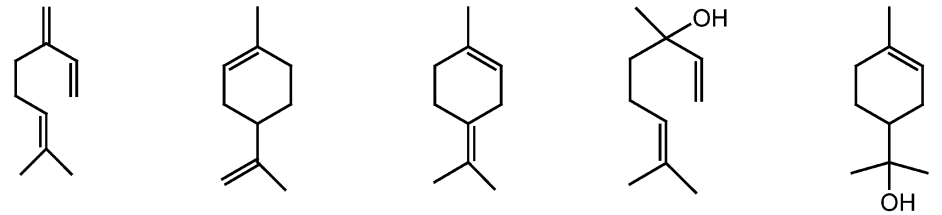
Table 1. Ratios Obtained for CH_3ReO_3-Catalyzed Isomerization of Geraniol

Reactant	Desired product		CH_3ReO_3[a]	CH_3ReO_3[b]
		Time	Yield	Yield
		2.5d	86%	
		12 h		62%
		1 d		65%
		2.5 d		40%

Products obtained at the end of 2.5 d



2 (94)[C] 12 (94)[C] 6 (96)[C] 22 (96)[C] 16 (96)[C]

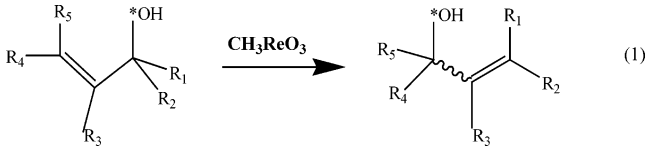
[a] Data based on NMR as reported in ref 1. Conditions: 5 mM MTO, 50 mM substrate. [b] Yield as determined in GC-MS spectra, 5 mM MTO, 50 mM reactant in dry C_6H_6. [c] The first number refers to the quantity of compound present relative to the internal standard obtained by GC. The final amount of linalool produced was 40% of the initial concentration of geraniol. The number in parentheses is the "Similarity Index", which is a quantitative measure of the difference between the patterns in the mass spectrum of an unknown and a spectrum registered in a library (100 is identical, 0 if completely different). The library used in this report is the NIST 98 Mass Spectral Database.

%) or 1.5 μL of 2 M $HClO_4$ (1 mol %) were stirred at room temperature for 3 days and the reaction monitored by GC-MS periodically over the reaction period.

3. Results and Discussion

3.1. Extent of Isomerization. First, we examined a catalytic reaction between CH_3ReO_3 and the allylic alcohol geraniol under the same conditions described in the previously published paper (see Table 1).[1] The extent of isomerization we obtain is significantly different from the published one, and we conducted several trials with this alcohol. After 2.5 days under similar conditions our extent of isomerization at 40% is much less than the 86% reported previously.[1] Our yields were determined using GC-MS and quantified by employing cyclooctane as an internal standard. The percent conversion of product was obtained by interpolation from the average value of the results from a calibration curve of the specific product, which had an r^2 value of 0.99. Those reported previously[1] appear to have been obtained from integration of NMR spectra, and this may account for the higher reported yield. The best quantity for the geraniol (see Table 1) and CH_3ReO_3 was 65% after 1 day. Leaving this mixture for 2.5 days resulted in the formation of other isomerized and dehydrated products (see Table 1) and in a decrease of the isomerized alcohol (i.e., linalool) to 40%.

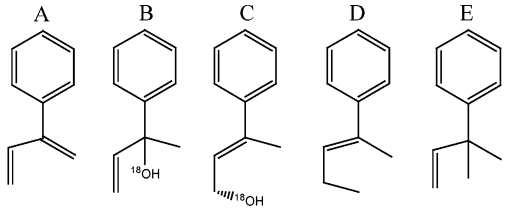
3.2. Mechanism of the Isomerization Reaction. The 1,3-transposition of allylic alcohols (eq 1) accomplished with CH_3ReO_3 was suggested to go via transfer of the oxygen atom on the alcohol and not involve metal-bonded O atom transfer.[1] This was based on labeling studies where ^{18}O-enriched CH_3ReO_3 was used and no ^{18}O ended up on the alcohol that had isomerized. We conducted a catalytic reaction between ^{18}O-enriched



(1)

2-phenyl-3-buten-2-ol (44% ^{18}O; Figure S1 in the Supporting Information) and CH_3ReO_3. After the maximum yield of product was attained (by comparison to an internal standard), the abundances of ^{18}O in the starting and isomerized alcohols were 32% and 15%, respectively (Figures S2 and S3 in the Supporting Information,, respectively). Table 2 lists the full range of compounds

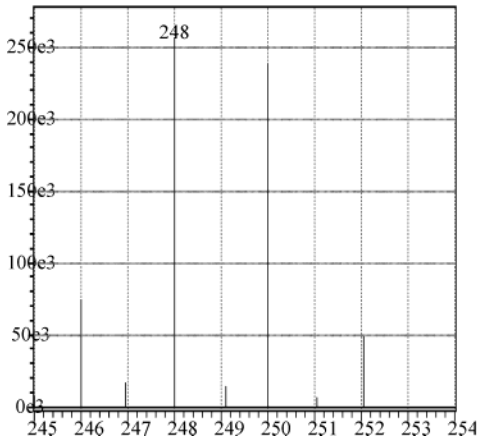
Table 2. Compounds Present from MTO-Catalyzed Isomerization of 44% ^{18}O-Enriched 2-Phenyl-3-buten-2-ol[a]



17.4 (96) 7.0 (84) 17.0 (85) 11.5 (81) 14.1 (85)

[a] The number below each drawing refers to the quantity of compound present relative to an internal standard obtained by GC. The number in parentheses is the Similarity Index; see footnote *c* in Table 1.

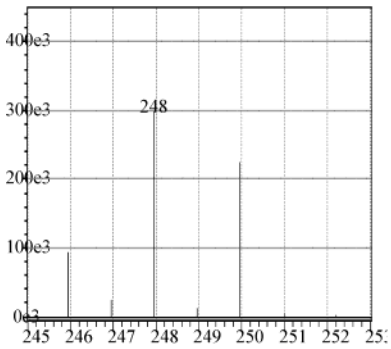
obtained in this catalytic experiment when the aforementioned percentages were obtained. In addition to the desired isomerized compound (i.e., compound C), in this case we also have a dehydrated compound, compound A, and two isomers, compounds D and E, where the port conditions may have resulted in forming these com-



[MS Spectrum]
# of Peaks 7
Raw Spectrum 2.993 (scan : 88)
Background No Background Spectrum
Base Peak m/z 250.00 (Inten : 237,994)

m/z	Absolute Intensity	Relative Intensity
246.00	73601	30.93
246.95	15855	6.66
248.00	256123	107.62
249.10	13459	5.66
250.00	237994	100.00
251.05	6167	2.59
252.05	47872	20.11

Figure 1. MS isotopic profile for MTO after reaction.



[MS Spectrum]
# of Peaks 7
Raw Spectrum 3.089 (scan : 105)
Background No Background Spectrum
Base Peak m/z 249.95 (Inten : 224,393)

m/z	Absolute Intensity	Relative Intensity
245.95	92966	41.43
246.95	22392	9.98
247.95	297264	132.47
248.95	11184	4.98
249.95	224393	100.00
251.00	3715	1.66
252.20	1603	0.71

Figure 2. Actual isotopic profile of initial MTO.

pounds (as this was under catalytic conditions) and/or a methyl group may have been transferred from CH_3ReO_3, perhaps in an exchange with the hydroxyl group. It is noteworthy that we did not observe such methyl group exchange with the study involving geraniol, and the appearance of these compounds (i.e., D and E in Table 2) is not definitive proof of this.

Moreover, mass spectroscopy showed an increase of ^{18}O in CH_3ReO_3 from 0.7% to 17% at *m*/*z* 252 (assigned to $CH_3{}^{187}Re(^{18}O)O_2$) and the ratio *m*/*z* 248/250 (Figure 1) is significantly different from that of the MTO itself (Figure 2). This result suggests that O atom exchange is moving toward a random distribution of the ^{18}O atoms among three sites on CH_3ReO_3 and one on the allylic alcohol. Clearly, the formation of the other products shown in Table 2 would prevent the reaction from attaining an ideal distribution of ^{18}O atoms. This distribution was also approached when reacting CH_3ReO_3 with ^{18}O-enriched alcohol at a lower concentration. We conducted a stoichiometric reaction between ^{18}O enriched 2-phenyl-3-buten-2-ol (7.6% ^{18}O; Figure S4 in the Supporting Information) and CH_3ReO_3. After the reaction, the abundances of ^{18}O in the starting and isomerized alcohols were 3.4% and 2.8%, respectivel (Figures S5 and S6 in the Supporting Information, respectively). This again suggests O atom exchange, as these numbers are heading toward a random distribution of the ^{18}O atoms among the four sites. Further, GC-MS analysis showed an uptake of ^{18}O isotope in CH_3ReO_3 at *m*/*z* 252. The spectrum revealed that the relative abundance of the *m*/*z* 252 ion increased from 0.7% initially (Figure 2) to 5.0% after equilibrium was attained (Figure S7 in the Supporting Information). The error in the measurements for the isotopic profiles can be estimated to be ±0.8% (see p 8 in the Supporting Information).

The isotopic profile of CH_3ReO_3 should contain molecular peaks $CH_3ReO_3^+$ at *m*/*z* 248 and 250 corresponding to species containing ^{185}Re and ^{187}Re, respectively. However, overlapping of the $CH^{187}ReO_3^+$ fragment with the $CH_3{}^{185}ReO_3^+$ ion at *m*/*z* 248 results in an *m*/*z* 248/250 ratio for the measured isotopic profile (Figures 1 and 2) different from that of the calculated spectrum (Figure S8, Supporting Information).[8] The *m*/*z* 246 peak can be assigned to the fragment $CH^{185}ReO_3^+$, and the peak at *m*/*z* 252, initially at a relative intensity of 0.71, is due to $CH_3{}^{187}ReO_2{}^{18}O^+$ (see Table 2). After a reaction period of 4 days, the relative intensities of peaks were changed and the significant increase of the peak at *m*/*z* 252 (5.0%) is good evidence that CH_3ReO_3 obtained ^{18}O from allylic alcohol. An increase in this *m*/*z* 252 peak was also noted in a repeat of this experiment measured after 1 day. The possible fragments which correspond with the major mass units from Figures 1 and 2 and Figure S8 are proposed in Table 3.

These results, i.e., the change in ^{18}O isotope concentration in the starting and isomerized alcohol and the incorporation of ^{18}O in CH_3ReO_3, suggest that the mechanism of 1,3-transposition of allylic alcohol catalyzed by CH_3ReO_3 occurs via the transfer of the metal-bonded O atom to alcohol, as shown in eq 2, was as initially suggested.[1]

To rule out proton catalysis as a contributor to the isomerization, experiments between a proton donor and allylic alcohol were conducted. Hydrochloric acid and

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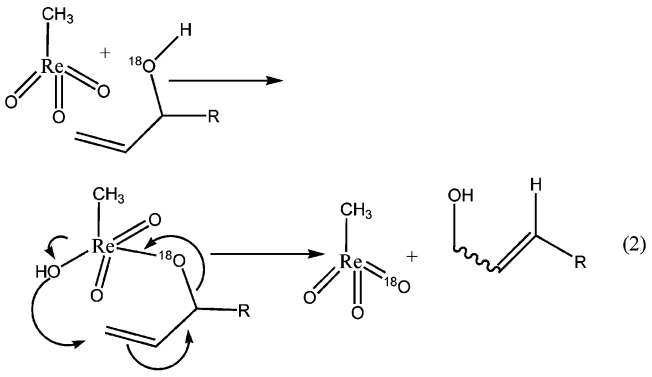
Table 3. Suggested Fragments for Major Mass Units from MS Spectra

	m/z 246	*m/z* 248	*m/z* 250	*m/z* 252
expected isotope of CH_3ReO_3		$CH_3{}^{185}ReO_3{}^+$	$CH_3{}^{187}ReO_3{}^+$	
actual isotope of initial CH_3ReO_3	$CH^{185}ReO_3{}^+$	$CH_3{}^{185}ReO_3{}^+$ $CH^{187}ReO_3{}^+$	$CH_3{}^{187}ReO_3{}^+$	
actual isotope of CH_3ReO_3 after reaction	$CH^{185}ReO_3{}^+$	$CH_3{}^{185}ReO_3{}^+$ $CH^{187}ReO_3{}^+$ $CH^{185}ReO_2{}^{18}O^+$	$CH_3{}^{187}ReO_3{}^+$ $CH^{187}ReO_2{}^{18}O^+$ $CH_3{}^{185}ReO_2{}^{18}O^+$	$CH_3{}^{187}ReO_2{}^{18}O^+$



(2)

perchloric acid were selected as proton sources. Stoichiometric and catalytic reactions (1 and 10 mol % acid) were conducted, and the GC-MS results did not reveal any significant concentration of isomerized products. The use of acid mainly results in the expected dehydrated compound and other compounds not observed in the reactions with CH_3ReO_3 (Charts S1−S5 in the Supporting Information). The nature of some of the products has been tentatively assigned using the Similarity Index measure (based on the NIST 98 LIB[9]). While these assignments are not conclusive, no isomer with retention times similar to those produced in reactions using CH_3ReO_3 was obtained. This suggests that adventitious variation in the concentration of proton donors should not be considered as playing a major role in the ^{18}O-labeled study of this isomerization.

Interestingly enough, in an attempt to see if the reverse reaction pertains, i.e., if ^{18}O can detach from ^{18}O-enriched CH_3ReO_3 and end up on the alcohol, $CH_3Re^{16}O_3$ (20 mg) was subjected to 10% $H_2{}^{18}O$ (0.5 mL) for 4 h. In one experiment after this solution was pumped to dryness overnight, the material left behind appeared to be a mostly dark green-gold material, presumably what was referred to as "poly-CH_3ReO_3"; namely, $\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}_\infty$.[10] Benzene was added to this solid and the resulting solution filtered, yielding a clear and colorless solution (no evidence of CH_3ReO_3 in this solution via mass spectroscopy) and a green-gold residue. This residue was capable of rapid allylic alcohol (geraniol) isomerization, without incorporation of ^{18}O in the isomerized (linalool) and starting alcohol (both 70% conversion after 1 h). The fast rate at which this isomerization occurs is interesting, as CH_3ReO_3 took 12 h to accomplish a 62% conversion in our hands and reportedly 2.5 days to accomplish an 86% conversion.[1] Therefore, if the initial CH_3ReO_3 was still present in the residue material after attempts to produce ^{18}O-enriched CH_3ReO_3, it may not be able to compete to transfer ^{18}O in the presence of this more active catalyst. Experiments using ^{18}O-enriched 2-phenyl-3-buten-2-ol (with CH_3ReO_3 subjected to $H_2{}^{16}O$) revealed no reduction in the concentration of ^{18}O (in the alcohol), suggesting that 1,3-transposition occurred with this residue without O atom exchange. This experiment suggests a reason for the apparent difference between our results (using unaltered CH_3ReO_3) and those reported earlier where the labeling experiments involved subjecting CH_3ReO_3 to water.[1]

4. Conclusions

A variety of products are obtained when CH_3ReO_3 is used as the catalyst to isomerize allyl alcohols. These include dehydrated compounds, other isomers of the starting material, and in some cases, products indicating methyl group transfer from CH_3ReO_3 may have occurred. The mechanism for isomerization of allylic alcohols using CH_3ReO_3 appears to occur via transfer of the metal-bonded O atom to the alcohol. This was established on the basis of the ratios of products obtained using ^{18}O isotope labeled alcohol, where the percentage of ^{18}O atoms on the alcohol decreased and that on the Re atom increased. Isomerization reactions carried out in the presence of acid contained products (and none of the desired isomers) different from those obtained with CH_3ReO_3, ruling out adventitious protons as the reason for this difference. A mechanism where CH_3ReO_3 acts as a Lewis acid to heterolyze the C−O bond, followed by collapse of the ion pair or migration of the allylic cation to another molecule of CH_3ReO_3, which would result in the loss of label from substrate and incorporation of label onto CH_3ReO_3, has not been ruled out in this study.[11] Experiments with CH_3ReO_3 after treatment with water suggests that a more active form, presumably "poly-CH_3ReO_3", may be causing the isomerizations without O atom exchange. This provides an explanation for the apparent discrepancy between our findings and those published earlier.

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Supporting Information Available: Figures of mass spectra referred to in the text and tables and text giving analyses of the isotopic patterns, results with acids, and details of the preparation of ^{18}O-enriched acetophenone. This material is available free of charge via the Internet at http://pubs.acs.org.

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