1,3-Transposition of Allylic Alcohols Catalyzed by Methyltrioxorhenium

Josemon Jacob, James H. Espenson,* Jan H. Jensen, and Mark S. Gordon*

Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

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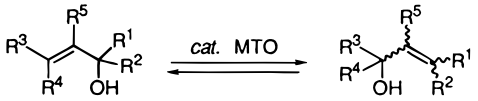
Methyltrioxorhenium (MTO) catalyzes the 1,3-transposition of allylic alcohols to generate the more stable isomer at equilibrium. The direction of the equilibrium is largely decided by the nature of the OH group, i.e., whether it is primary, secondary, or tertiary. In the case of aliphatic allylic alcohols, tertiary is preferred to secondary which is preferred to primary. For aromatic allyl alcohols, the more conjugated isomer predominates largely at equilibrium. Oxygen-18 labeling showed that the OH groups of the parent and product are the same. The reaction is first order with respect to both allyl alcohol and MTO but strongly inhibited by traces of water. Theoretical calculations suggest the same results in the case of aliphatic allyl alcohols, although aromatic allyl alcohols do not follow the predictions. Studies of deuterium-labeled substrates show a large *equilibrium* isotope effect ($K = 1.20 \pm 0.02$). For isomeric allyl alcohols differing in the position of deuterium only, the isomer with the deuterium at the sp^3 center predominates at equilibrium. The effect of conjugation from a phenyl group appears to be less important since calculations suggest that the phenyl group is forced out of plane of the allylic π system.

Introduction

Functional-group transpositions[1,2] contribute an important technique to supplement the formation of carbon−carbon bonds and the interconversion of functional groups, which constitute the substance of much synthetic work. We shall address here a rearrangement of allylic alcohols that converts one isomer to another, related by a 1,3-transposition of the OH group. The conversion can be complete or partial, depending on the spontaneity of the reaction. Such rearrangements do not occur on their own, however, and the role played by a particular catalyst is of considerable fundamental interest. The utility of this transposition arises when the more readily accessible allylic alcohol is not the desired one. A chemical equation for the general case, ignoring issues of regioselectivity to be addressed later, is given in eq 1.



(1)

Early studies of the synthesis of vitamin A represent pioneering investigations of the use of allylic rearrangements in the natural products area. The sulfuric-acid-catalyzed rearrangement of one allylic alcohol to its more conjugated isomer was used in the original C_{14}−aldehyde route to vitamin A.[3,4] Multiple allylic rearrangements are characteristic features of vitamin A synthesis.[5,6] Allylic transpositions of the oxygen functionality have found wide applications in many other natural product areas.[7−10]

The classical method for equilibrating an allylic alcohol or ester is with a strong protic or Lewis acid catalyst.[6,9−18] In favorable cases, this method succeeds splendidly and near quantitative yields have been obtained.[6] More typically, however, the yields are only moderate, the allyl cation intermediates being diverted in part along other reaction pathways.[11] Side reactions typically encountered are elimination to yield dienes,[12] skeletal rearrangements,[13] cyclization,[14] and the formation of resinous materials.[11,15] Herein, we report the use of the Lewis acid methyltrioxorhenium (CH_3ReO_3, abbreviated as MTO) to effect allylic transpositions in a single step.

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In recent years, MTO has received much attention as a versatile homogeneous catalyst for various transformations. The ability of MTO to activate hydrogen peroxide has made it a very useful catalyst for olefin epoxidation and other selective oxidations.[16−23] Nonoxidative transformations catalyzed by MTO include its use to activate diazo reagents,[24] oligomerize aldehydes,[25] convert epoxides and carbonyl compounds to 1,3-dioxolanes,[25] olefinate aldehydes,[26] and metathesize alkenes.[27]

Results and Discussion

Reactions. Benzene was chosen as the solvent primarily because MTO is especially stable in it. Indeed, in all of the transpositions described in this work, many of which required reaction times on the order of days, no decomposition of the catalyst was noted. Acetonitrile was used as the solvent in a few instances, but its use led to a mild prolongation of the reaction. Most data were obtained in benzene for the aforementioned reason.

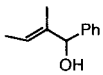
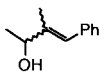
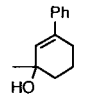
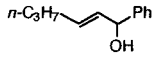
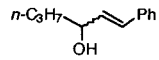
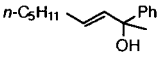
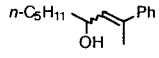
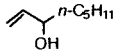
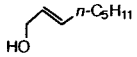
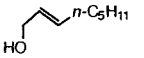
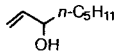
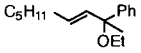
In a generic sense, all of the reactions are the same, resulting in the transformation of one allylic alcohol to another, the consequence of a 1,3-shift of the OH group with accompanying migration of the double bond. These are the features represented in eq 1.

The major results refer to 14 primary (1°), secondary (2°), and tertiary (3°) allylic alcohols. Both aromatic and aliphatic allylic alcohols were investigated to understand the nature of these isomerizations. The products formed, their yields, and the reaction times required are presented in Table 1. Several of the reactions were nearly quantitative: see entries 2−5. The other cases gave lesser yields, which might be attributed to decomposition/deactivation of the catalyst, to an insufficient reaction time, to side reactions consuming the catalyst, or to the attainment of chemical equilibrium. A proper understanding of this system required that each possibility be explored.

In all cases, MTO was detected by ^{1}H NMR at the end of the allotted time: it remained intact at essentially the initial concentration, clearly ruling out catalyst decomposition/deactivation. Also, any deactivation by polymerization of MTO can be ruled out since low concentrations of catalyst (5 mM) were used.[34] To check this further, additional MTO was added after the allowed time in one experiment, entry 10, but no additional product was formed. Had sufficient time been allowed? These reactions were checked intermittently by NMR, prior to the reported reaction time and after. The buildup of product to a certain level (only) was seen, but waiting longer gave no increase in yield.

We thus turned to another explanation. In certain cases (see entries 6, 7, and 11), the byproducts were irreversibly formed. Once they were allowed for, mass balance was satisfactory; little starting material re-

Table 1. Yields Obtained for MTO-Catalyzed Isomerizations of Allylic Alcohols[a]

Entry	Substrate	Product	Time	% Yield
1			5 d	63
2			4 d	90[b]
3			12 h	93
4			10 h	98
5			1 d	98
6			2 d	65[c]
7			2 d	67[d]
8			3 d	52
9			1 d	33
10			3 d	61
11			2.5 d	86[e]
12			2 d	30
13		No rxn		
14		No rxn		
15			2.5	87

[a] Reactions carried out in benzene with 5% MTO catalyst. [b] 4:1 ratio of *Z* and *E* isomers were obtained. [c] 35% of the dehydration product was also observed, eq 3. [d] ∼30% of the ether product was also observed, eq 2. [e] 7% of the dehydration product also observed.

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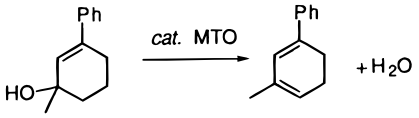
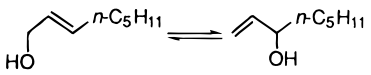
mained. The side reactions responsible are well-known and also require MTO as a catalyst; they consist of condensation (entry 7, eq 2) and dehydration of the product (entry 6, shown in eq 3, and entry 11).

$$2\mathrm{ROH} \xrightarrow{\text{cat. MTO}} \mathrm{ROR} + \mathrm{H_2O} \quad (2)$$



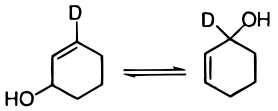
(3)

The attainment of chemical equilibrium can also account for lower yields. This is best illustrated by data, entries 9 and 10, with 1-octene-3-ol and 3-octene-1-ol. They are the products of one another's reactions. Both systems come essentially to the same point, and the mass balance is satisfactory (94%). The equilibrium constant for reaction 4 from these data is $K_4 = 1.7 \pm 0.2$ in benzene at ~23 °C.



(4)

An independent examination of the attainment of equilibrium was sought with a compound for which the 1,3-transposed pair would be the same. These experiments were carried out with 2-cyclohexen-1-deutero-1-ol. They are interconverted by a degenerate reaction, as shown in eq 5.



(5)

The equilibrium was approached starting from 2-cyclohexen-1-deutero-1-ol and can be easily followed by NMR for the growing proton of the carbon bearing the OH group. Several independent investigations gave the same result. The amounts of the two species at equilibrium are similar but not identical. This can be expressed as an equilibrium constant, $K_5 = 1.20 \pm 0.02$ in benzene at ~23 °C. In other words, this equilibration shows an appreciable *equilibrium isotope effect*. We shall return to discuss this among the theoretical results.

The reaction is found to be very sensitive to the presence of water. Deliberate addition of water (0.25 mol %) to entry 9 showed that the isomerization was greatly inhibited in the presence of water (the control reaction gave 25% of rearranged isomer in 16 h, whereas in the presence of added water there was only 5% of rearranged isomer at the same time). The reaction times needed to attain equilibrium from each direction were different: 1 and 3 days (entries 9 and 10). This, on face value, poses a formidable problem in that the lifetime for the attainment of equilibrium should be the same starting from either side: $\tau = (k_f + k_r)^{-1}$. The difference in this case arises from a trivial source, because of the sensitivity of the reaction rate to traces of water, which was not rigorously controlled. The strong retarding effect of water will be considered further in the section on kinetics.

We also checked to see whether the catalyst is still active after the equilibration is reached. In a kinetic experiment which was followed by ^{1}H NMR, the isomerization of 3-methyl-2-buten-1-ol (50 mM) with 25 mM MTO was monitored. After the attainment of equilibrium between the two isomeric allylic alcohols, a second batch of 3-methyl-2-buten-1-ol (50 mM) was added. The experimental trace is shown in Figure 1. In fact, the rate constants agree very well for the two stages of the reaction.

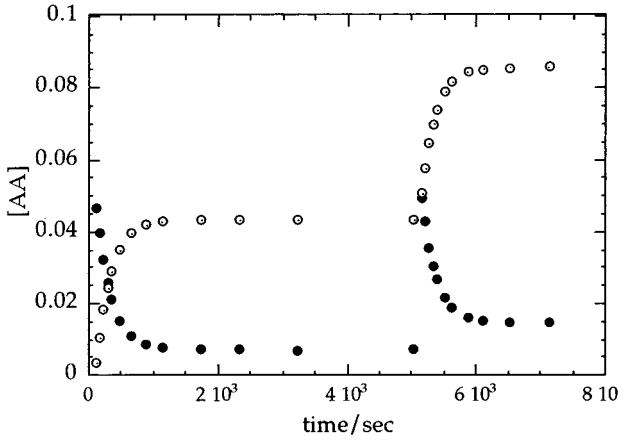


Figure 1. Kinetic trace obtained by NMR spectroscopy for the isomerization of 3-methyl-2-buten-1-ol (decreasing with time) to 2-methyl-3-buten-2-ol (increasing with time). [MTO] = 25 mM, [AA] = allyl alcohol = 50 mM. The second stage of the reaction indicates a second addition of 3-methyl-2-buten-1-ol.

Reaction Kinetics. To define the mechanism, we carried out a series of kinetic studies using 3-methyl-2-buten-1-ol as the test substrate. The reaction was monitored by ^{1}H NMR under varying concentration conditions. In every case, the reaction followed exact first-order kinetics. One series of kinetic experiments in C_6D_6 at room temperature was carried out at a constant concentration, 50 mM, of allyl alcohol. The rate constants obtained at various catalyst concentrations are as follows:

[MTO]/mM:	25	40	75	100
$k/10^{-3}$ s^{-1}:	1.53	2.40	4.58	5.94

The plot of k vs [MTO] defines a straight line that passes through the origin, as shown in Figure 2. The slope of this line, 0.060 L mol^{-1} s^{-1}, is the second-order rate constant for the reaction between 3-methyl-2-buten-1-ol and MTO.

There is, however, an alarming effect of changing the concentration of the allyl alcohol substrate. The following data for 3-methyl-2-buten-1-ol, taken at 25.0 mM MTO, illustrate the situation.

[AA]/mM:	50	100	200	300
$k/10^{-3}$ s^{-1}:	1.53	2.72	1.29	0.55

That is, the rate constant decreases with increasing substrate concentration despite the excellent fit to first-order kinetics in each separate experiment. We could identify no kinetic scheme, plausible or otherwise, to account for this set of facts. We also examined the reproducibility of the kinetic data, which was satisfactory among experiments carried out any 1 day. On other days, variations of the rate constant by factors of 2−4 were not uncommon. Again, the effect of uncontrollable amounts of water seem to be the limiting

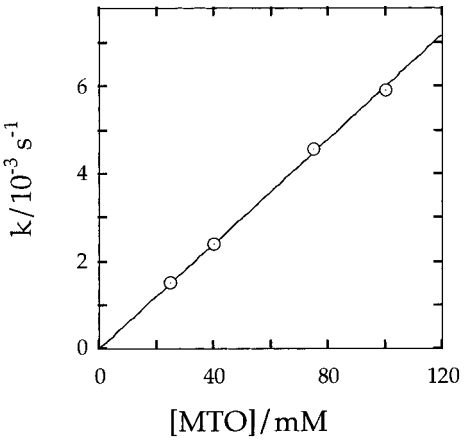


Figure 2. Kinetics of the rearrangement reaction of 3-methyl-2-buten-1-ol at varying concentrations of MTO and a fixed concentration of allyl alcohol, 50 mM. The data are displayed as a plot of *k* vs [MTO], which defines a straight line that passes through the orgin.

factor, just as it was in the previously described equilibration reactions for entries 9 and 10.

Despite these limitations, the data are nonetheless important to defining the reaction orders in the system. The data presented are internally consistent; they are also indicative of the approximate rate constants, within the factors cited.

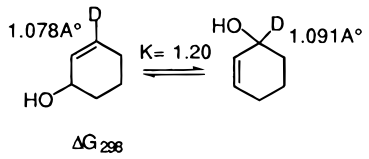
Attempts to detect two catalyst species, free and bound, by NMR in acetonitrile at low temperature did not succeed. Only allylic alcohols undergo this isomerization with MTO. When a bishomoallylic alcohol (entry 13) was used, no transposition of the OH group was observed. Also, allylic ethers (entry 14) do not undergo any isomerization.

^{18}O-Labeling Experiment. Experiments were carried out to trace the origin of the oxygen atom of the rearranged allyl alcohol, in particular to learn whether it comes from MTO. To test this mechanism, ^{18}O-labeled MTO was prepared by allowing MeRe(^{16}O)$_3$ to equilibrate in 95% $H_2{}^{18}O$ at room temperature for 4 h. The MTO was then extracted into dichloromethane. GC-MS analysis showed a high level of ^{18}O incorporation in MTO. A *stoichiometric* reaction between 3-methyl-2-buten-1-ol (entry 15 in Table 1) and MeRe(^{18}O)$_3$ (both at 25 mM) was run in C_6D_6. These particular procedures were adopted to minimize the exchange that might result after numerous catalytic turnovers. After equilibration, the reaction was analyzed by GC-MS by both CI and EI ionization methods. No ^{18}O incorporation into the rearranged allyl alcohol was observed; 2-methyl-3-buten-2-ol showed only *m*/*z* 86 and no *m*/*z* 88).

Theoretical Results. Three factors need to be considered to understand the direction of equilibrium in these reactions: (a) the position of the OH group, (b) the nature of the double bond, i.e., more substituted or less substituted, and, (c) the effect of conjugation. To clarify these points, we adopted a theoretical approach to study these effects. The results are discussed below.

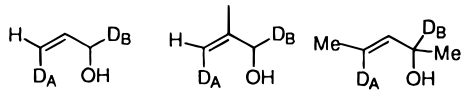
For the isotope substitution studies, we predict a ΔG_{298} difference of about 0.1 kcal/mol for the structures favoring substitution at the longest C−H bond (sp^3 vs sp^2). Calculations relating to the thermodynamics of different isotopic substitution on different substrates are

Scheme 1



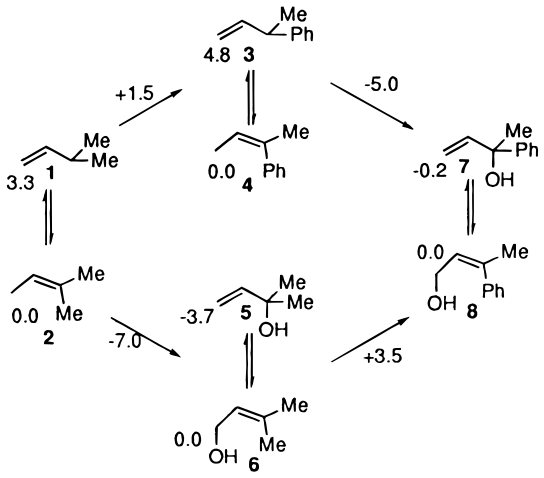
RHF/DZP: 0.12 kcal/mol 0.0 kcal/mol

Scheme 2 ΔG_{298} Relative to D_B



RHF/DZP: 0.10 0.09 0.11 kcal/mol

Scheme 3 ΔG_{298} (kcal/mol) Values Obtained Using MP2/DZP+//RHF/DZP

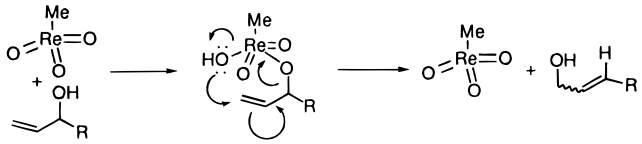


shown in Schemes 1 and 2. Calculations on all four of these substrates suggested a ΔG difference of 0.1 kcal/mol in favor of deuterium at the sp^3 center. This agrees with the experimental observation for the substrates shown in Scheme 1 for which the equilibrium constant was found to be 1.20, corresponding to a ΔG value of 0.11 kcal/mol.

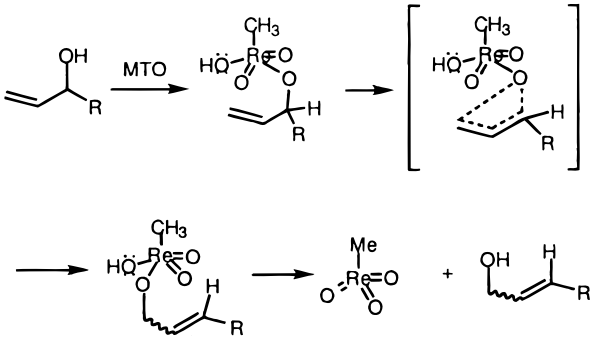
We chose entries 2 and 15 on Table 1 to study the effect of various factors mentioned above on the direction of equilibrium. The results are summarized in Scheme 3. The parent equilibrium between **1** and **2** lies toward the more substituted olefin by 3.3 kcal/mol. This value seems converged with respect to correlation and the basis set: MP2/DZP+ = 3.3 kcal/mol, MP2/aug-cc-p VDZ = 2.9 kcal/mol, and MP4/DZP = 3.0 kcal/mol. The addition of the OH group reverses the equilibrium (between **5** and **6**), while addition of the phenyl group favors substitution at the olefin. The calculations suggest two interesting things about **8**: (1) the *Z* form is lower in energy than the *E* form by 1.0 kcal/mol, and (2) the two π systems are not in the same plane and the planar structure is a transition state to rotation about the C−Ph bond ($\Delta G^{\ddagger}_{298}$ = 7.8 and 2.8 kcal/mol for the cis and trans form of **8**, respectively).

The calculations suggest that the two isomers in entry 2 are essentially isoenergetic, whereas experiment predicts a 1.3 kcal/mol energy difference, favoring **8**. Currently, no level of theory can consistently guarantee a <1 kcal/mol deviation from experiment for these

Scheme 4. Suggested Mechanism



Scheme 5. Alternative Mechanism



relatively large systems. However, the main conclusion to be drawn from Scheme 3 regarding the entries in Table 1 is that they represent the balance of two competing substituent effects: substitution at the alcohol or olefin site. In the case of alkyl substituents, the effect of substitution at the OH site dominates the effect of substitution at the olefin site (see entries 9−12). According to Scheme 3, this dominance at the OH site is almost but not quite canceled when one alkyl substituent is replaced by a phenyl substituent, while experiment suggests that this replacement does shift the dominance to the olefin site (see entries 1−8). It is the shift in dominance between two competing effects on going from alkyl to phenyl substituents that predicts a simple explanation of the results shown in Table 1 in terms of 1°, 2°, and 3° alcohols.

Reaction Mechanism. Previous work has shown that MTO readily forms complexes with alcohols and diols.[28] Many stable complexes have been isolated and reported in the literature.[29,30] The −OH group adds across a Re═O bond, just as it does in the reaction between MTO and hydrogen peroxide. This seems a reasonable place to begin to consider the mechanism. In the first step, MTO most likely forms a monoalkoxy complex with the allylic alcohol. Scheme 4 presents one plausible mechanism. Similar mechanisms using oxometal complexes have been suggested in the literature.[31,32] The rearranged isomer can be envisaged as being readily obtained from this initially formed complex by a suitable migration of bonds, Scheme 4.

To our surprise, and in contradiction to Scheme 4, no ^{18}O incorporation was observed in the rearranged allyl alcohol. We, thus, suggest an alternative mechanism depicted in Scheme 5.

The transformation shown in Scheme 5 accounts for the labeling experiment and for the finding of second-order kinetics. A second allyl alcohol is not involved in the scheme. We speculate that the inhibiting role of water is to compete with the allyl alcohol in the first step, producing a dead-end species $MeRe(O)_2(OH)_2$. The reversible formation of this species accounts for the rapid O-18 exchange between MTO and water, and it parallels the peroxo complexes formed in reactions between MTO and H_2O_2. Evidently, it interferes with the allyl alcohol by reducing the concentration of the active form of the catalyst.

Conclusions. MTO catalyzes the 1,3-transposition of allylic alcohols in a single step. For benzylic alcohols, the more conjugated isomer predominates at equilibrium. Quantum mechanical calculations suggest that the direction of equilibrium is determined by a competition for substitution at the alcohol or olefin site. For alkyl substituents, the more heavily substituted alcohol is favored (entries 9−12, 15). For phenyl substituents, the more conjugated structure is favored. The effect of conjugation appears to be less significant than expected since the phenyl group is forced out of the plane of the allylic π bond.

Experimental Section

Materials. The allyl alcohols used in this study were obtained from commercial sources or synthesized according to literature procedures.[33−37] Their purities were checked by ^1H and ^{13}C NMR and by GC-MS. Benzene-d_6, obtained commercially, was dried by distillation over CaH_2 prior to use. The NMR spectra were measured at 300 MHz for protons with Me_4Si as an internal standard.

General Procedure. All experiments were done in benzene-d_6 with a 50 mM substrate concentration and 5 mM catalyst at room temperature. The reactions were followed by NMR and analyzed by GC-MS on attaining equilibrium. The yields were determined by proton integration relative to solvent or Me_4Si. The spectral data are in good agreement with the accepted values.[38,39]

Computational Methodology. All structures were optimized at the RHF level of theory using the Dunning−Hay polarized double-ζ (DZP) basis set.[40] All structures were shown to be minima (transition states) by analytically computing vibrational frequencies and verifying that none were (only one was) imaginary. Relative energies were computed using second-order Moller−Plesset (MP2)[41,42] perturbation theory using the DZP basis set augmented with a diffuse sp shell on each non-hydrogen atom (denoted DZP+).[43] Selected relative energies were also calculated using MP2 with Dunning's augmented correlation-consistent polarized valence double-ζ (aug-cc-p VDZ)[44] basis set, using fourth-order MP theory (MP4)[45] with the DZP basis set. The free energies were computed within the rigid rotor−harmonic-oscillator approximation. All calculations were done with the program

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GAMESS,[46] with the exception of the MP4 calculations which were done with GAUSSIAN 92.[47]

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Supporting Information Available: NMR data (^{1}H and ^{13}C) for the starting materials and products (4 pages). Ordering information is given on any current masthead page.

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