

# Dehydration of 2-Methyl-1-cyclohexanol: New Findings from a Popular Undergraduate Laboratory Experiment

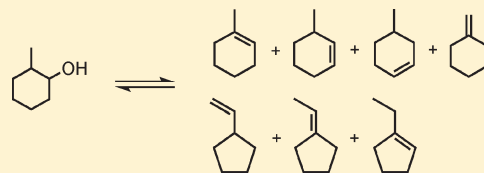
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**S** Supporting Information

**ABSTRACT:** The mineral acid-catalyzed dehydration of 2-methyl-1-cyclohexanol has been a popular laboratory exercise in second-year organic chemistry for several decades. The dehydration experiment is often performed by organic chemistry students to illustrate Zaitsev's rule. However, sensitive analytical techniques reveal that the results do not entirely corroborate with Zaitsev's rule. Previous reports pertaining to this experiment have been limited by two factors:

(i) it is difficult to separate 3- and 4-methyl-1-cyclohexene on a standard gas chromatography (GC) column and (ii) methods of accurate detection, identification, and quantification of trace minor products have been lacking. The current study uses gas chromatography–electron impact mass spectrometry (GC–MS) and quantitative nuclear magnetic resonance (qNMR) to identify and quantify not only the putative 1-, 3-, and 4-methyl-1-cyclohexene products but also several minor products such as methylenecyclohexane and ethylenecyclopentane. Performing the dehydration with a single diastereomer of 2-methyl-1-cyclohexanol reveals a striking difference between the product distributions associated with *cis* and *trans* isomers. Some evidence continues to point towards an E2-like mechanism whereas other evidence, such as the presence of methylcyclohexene dimers in the still pot, points towards E1 carbocation intermediates.



**KEYWORDS:** Second-Year Undergraduate, Laboratory Instruction, Organic Chemistry, Hands-On Learning/Manipulatives, Inquiry-Based/Discovery Learning, Elimination Reactions, Mass Spectrometry, NMR Spectroscopy, Reactions, Undergraduate Research

The phosphoric acid-catalyzed dehydration of 2-methyl-1-cyclohexanol, described by Price in 1939, has been a popular undergraduate organic chemistry experiment for several decades.<sup>1</sup> The classic dehydration of 2-methyl-1-cyclohexanol experiment was introduced in this *Journal* in 1967 by Taber.<sup>2</sup> Since that time, the experiment has retained its popularity in the organic chemistry laboratory curriculum. At the same time, the rather simple procedure of distilling an alcohol and aqueous mineral acid mixture has spawned several investigations that have resulted in American Chemical Society meeting presentations and peer-reviewed journal articles.<sup>3–7</sup> In 1987, Feigenbaum reported that the gas chromatography (GC) and nuclear magnetic resonance (NMR) analysis of the product mixture showed that both 1-methyl-1-cyclohexene and 3-methyl-1-cyclohexene were formed by the dehydration of 2-methyl-1-cyclohexanol in an 84/16 ratio.<sup>3</sup>

This same reaction resurfaced in this *Journal* in 1994 when Todd observed a kinetic effect that could be explained by proposing that in a mixture of *cis*- and *trans*-2-methyl-1-cyclohexanol the *cis* isomer reacts much faster than the *trans* isomer to give predominately 1-methyl-1-cyclohexene.<sup>4</sup> Todd also reported the formation of methylenecyclohexane. A follow-up study by Cawley and Lindner in 1997 produced a detailed kinetic study of this reaction.<sup>5</sup> In this investigation, students began with a 36.6/63.4 *cis/trans* mixture of 2-methyl-1-cyclohexanol. Distillate fractions and a sample of the still pot reaction mixture were collected at 4, 8, 16, 24, and 28 min. These fractions were analyzed by <sup>1</sup>H NMR and GC for alkene composition. The ratio

of *cis/trans* rate constants for the dehydration of reaction was determined to be 8.4 to one.

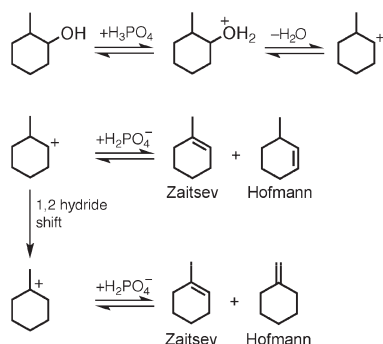
At first glance, the strongly acidic environment may be expected to sustain an almost quantitative yield of 1-methyl-1-cyclohexene owing to an E1 reaction mechanism that adheres to Zaitsev's rule. The presence of 3-methyl-1-cyclohexene may be explained by the formation of the Hofmann elimination regioisomer. In this mechanism, methylenecyclohexane, another Hofmann elimination product, is explained by the formation of a secondary carbocation and subsequent 1,2 hydride shift occurring prior to proton elimination from the methyl group as shown in Scheme 1.

A careful study of the reaction kinetics and product distribution offers evidence that the E1 mechanism does not completely explain the reaction outcomes. The rapid formation of 1-methyl-1-cyclohexene from *cis*-2-methyl-1-cyclohexanol relative to *trans*-2-methyl-1-cyclohexanol suggests an E2 synchronous anti-elimination of the  $\beta$  proton and the protonated alcohol.<sup>4,5</sup> Correspondingly, the dehydration of the *trans* isomer by the same mechanism would favor the formation of 3-methyl-1-cyclohexene by the same mechanism as shown in Scheme 2. The E2 mechanism helps to rationalize the kinetics between *cis*- and *trans*-2-methyl-1-cyclohexanol but is not helpful in explaining the formation of alkenes, such as methylenecyclohexane that could not occur by  $\beta$ -elimination.

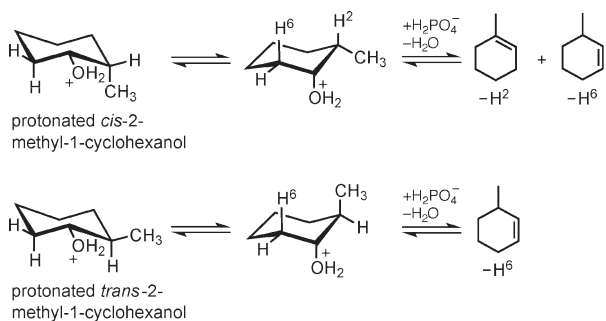
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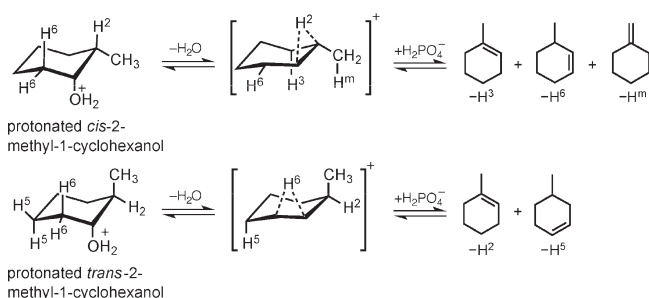
**Scheme 1. The Unimolecular Elimination (E1) Mechanism for the Formation of 1-Methyl-1-cyclohexene, 3-Methyl-1-cyclohexene, and Methylene-cyclohexane from the Phosphoric Acid-Catalyzed Dehydration of 2-Methyl-1-cyclohexanol**



**Scheme 2. The Bimolecular Elimination (E2) Mechanism for the Formation of 1-Methyl-1-cyclohexene and 3-Methyl-1-cyclohexene from *cis*-2-Methyl-1-cyclohexanol and *trans*-2-Methyl-1-cyclohexanol**

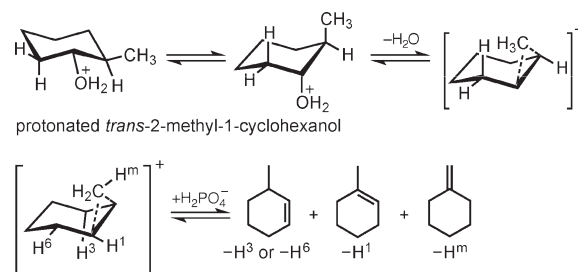


**Scheme 3. The Ethylene Protonium Ion Mechanism for the Formation of 1-Methyl-1-cyclohexene, 3-Methyl-1-cyclohexene, and Methylene-cyclohexane from *cis*-2-Methyl-1-cyclohexanol and *trans*-2-Methyl-1-cyclohexanol**

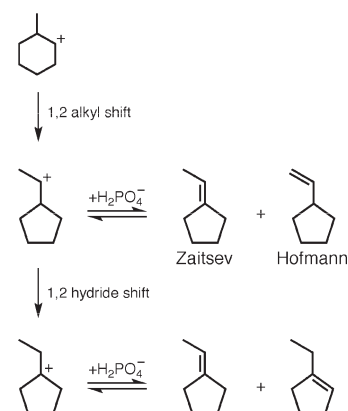


Another possible mechanism invokes the formation of a bridged protonium ion as a result of a  $\beta$ -assisted elimination of the protonated hydroxyl group.<sup>5</sup> This is a variation of the neighboring hydrogen participation to form ethylene protonium ions in the solvolysis of *p*-toluenesulfonate esters proposed by Cram and Tadanier in 1958.<sup>8</sup> Once the bridge is formed, the hydrogens adjacent to the bridged carbons may be

**Scheme 4. The Bridged Carbonium Ion Mechanism for the Formation of 1-Methyl-1-cyclohexene, 3-Methyl-1-cyclohexene, and Methylene-cyclohexane from *trans*-2-Methyl-1-cyclohexanol<sup>5</sup>**



**Scheme 5. The E1 Mechanism for the Formation of 1-Ethyl-1-cyclopentene, Vinylcyclopentane, and Ethylidenecyclopentane from 2-Methyl-1-cyclohexanol**

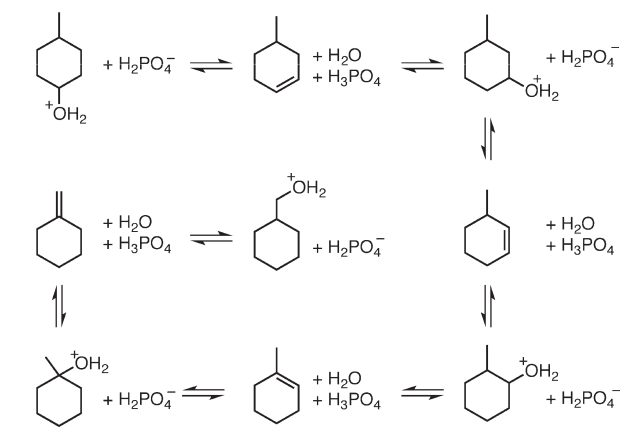


eliminated to form the alkene. From the point of view of molecular orbital alignment, it makes sense to propose that the eliminated hydrogen is the one most nearly anti-periplanar to the bridging hydrogen as shown in Scheme 3. The ethylene protonium ion intermediate can explain both the observed kinetics and the formation of the three most-often reported elimination products.

A carbonium ion bridge initiated by the methyl group has been proposed to explain the generation of methylenecyclohexane from *trans*-2-methyl-1-cyclohexanol as shown in Scheme 4.<sup>5</sup> The presence of 1-ethyl-1-cyclopentene and ethylidenecyclopentane has been reported among the 2-methyl-1-cyclohexanol dehydration products.<sup>6,7</sup> The E1 mechanism explanation involves a 1,2-alkyl shift from a secondary carbocation to form another secondary carbocation followed by proton elimination as shown in Scheme 5.

Several mechanistic pathways for the mineral acid-catalyzed dehydration of 2-methyl-1-cyclohexanol are evidently possible. Given the current limits of the studies performed, as well as the overlap of mechanistic outcomes, it is difficult to pinpoint a single most likely mechanistic pathway. The apparent inability to distinguish between 3- and 4-methyl-1-cyclohexene with reported GC methods is problematic in the product distribution analysis. Apparently, there have been no reports of performing this experiment with the separated *cis* and *trans* isomers even

**Scheme 6. The Dehydration–Rehydration Mechanism for the Interconversion of Isomeric Alkenes 1-, 3-, and 4-Methyl-1-cyclohexene, in Addition to Methylene-cyclohexane from 1-, 2-, 3-, and 4-Methyl-1-cyclohexanol as Well as Cyclohexylmethanol**



though they are commercially available. No evidence that the interconversion between these two diastereomers occurs under reaction conditions has been reported. In addition, sensitive detection techniques capable of identifying minor products and the presence of impurities in starting materials have been lacking in previous dehydration studies.

## EXPERIMENT OVERVIEW

Students are presented with the dehydration of 2-methyl-1-cyclohexanol as an example of an experiment that produces multiple products in varying proportions. A goal of this experiment was to involve undergraduate students in the discovery process related to mechanistic understanding. Students have access to previous student results; the previous experimental results have been posted on a public access wiki called "OChemOnline".<sup>10</sup> In this way, each year students seek to add to the body of knowledge associated with this experiment. Student-generated products are analyzed by advanced spectroscopic and spectrometric techniques to understand their complexity. The use of quantitative NMR (qNMR) to analyze the reaction products has the potential to resolve 3- and 4-methyl-1-cyclohexene as well as introduce a certain level of sensitivity. Quantitative NMR exploits the fact that each proton in an NMR experiment contributes equally to the area under the peak.<sup>7</sup> The utilization of highly sensitive GC–MS complements the qNMR analyses and allows the detection of minor products. The findings are used to evaluate existing mechanistic theories as well as explore new insights.

The analysis of the product distribution informs the experimenter of the mechanistic features of the reaction. Reaction mechanism, in turn, may be influenced by a number of experimental parameters such as, reactant molecular structure, reactant concentration, catalyst concentration, reaction time, and temperature. As part of their prelaboratory assignment, the students are introduced to the various aspects of the reaction such as the relative solubilities of reactants and products, the role of the acid catalyst, and the function of water (both solvent and reaction product). On the basis of the previous results, students are asked

to predict how a proposed modification will influence the outcome of the experiment. Students are asked to employ their understanding of reaction mechanisms, E1 and E2, to predict the change in outcome if reaction conditions are modified. The prediction explored here was the possibility that an equilibrium between dehydration and hydration played a significant role in the product distribution as shown in Scheme 6. In the present case, the modification was made by refluxing the reaction mixture before distilling off the alkene products.

Once the experiment has been performed, the students are asked to explain why the modification changed, or did not change, the results. As part of the laboratory report, students are also asked what further experiments should be performed to explore this phenomenon. In this way the undergraduate experiment becomes a research project that contributes to the accumulation of scientific knowledge

## EXPERIMENT

A 23 g portion of 1-methyl-1-cyclohexanol and 5 mL of 85% phosphoric acid were added to a 250 mL round-bottom flask. Two or three boiling chips were added to the flask and the flask was swirled to mix the layers. A reflux apparatus was constructed with 14/20 taper glassware round-bottom flask, Claisen adapter, reflux condenser, and thermometer adapter. A thermowell was used as a source of heat. The mixture was heated to boiling. After 10 min of reflux, the thermowell was removed by lowering it away from the round-bottom flask. A "Y" adapter and distillation condenser were inserted between the thermometer and Claisen adapter. A graduated cylinder was used to collect the distillate. The reflux condenser was replaced with a glass stopper. The mixture was heated to boiling a second time; the heat input was adjusted so that the temperature at the still head did not rise more than 10 °C above the boiling point of the expected alkene. The distillation was continued until there was about 5 mL of liquid left in the distilling flask. The distillate was transferred to a separatory funnel. The lower aqueous layer was drained off and discarded. The distillate was washed with one 15 mL portion of 5% sodium bicarbonate and one 15 mL portion of saturated aqueous sodium chloride. The crude organic product was transferred to a clean dry 50 mL Erlenmeyer flask and anhydrous magnesium sulfate (MgSO<sub>4</sub>) was added. The resulting mixture was filtered and the mass of the filtrate was recorded. Gas chromatography with flame ionization detection (GC-FID) was used to determine the composition and purity of the product.

## ANALYTICAL METHODS

Analysis of each fraction was performed on a Perkin-Elmer Clarus 600 GC-FID. The system is controlled through a desktop computer loaded with Totalchrom software. The analyses were performed on a 30 m Restek Stabilwax polyethylene glycol column with a 0.53 mm internal diameter (0.50 μm film thickness) and He as a carrier gas.

All <sup>1</sup>H NMR experiments were obtained on a 400 MHz Bruker AVANCE-400 spectrometer in 5 mm tubes using CDCl<sub>3</sub> as a solvent. The temperature was maintained at 25 °C. Chemical shifts (δ) were expressed in part per million (ppm) with reference to chloroform (δH 7.240). All NMR experiments were performed using standard Bruker pulse sequences. NMR processing used the NUTS software package (AcornNMR, Las Positas, CA), and line resolution of experimental data was enhanced by

**Table 1.** The GC-FID-Determined Products Obtained from the Distillate of Acid-Catalyzed Dehydration *cis/trans*-2-Methyl-1-cyclohexanol

Reflux	1-Methyl-1-cyclohexene (%)	3- and 4-Methyl-1-cyclohexene (%)	Methylenecyclohexane (%)
Without	83	14	3
With	82	15	3

Lorentz–Gauss (LG) transformation using individually determined parameters.

GC–MS was performed on a Varian quadrupole mass spectrometer equipped with an electron impact (EI) source, interfaced to a Varian CP-3800 gas chromatograph. The system was operated through a Varian Workstation 6.41 computer. Samples were analyzed on a HP-5 ms (5%-Phenyl)-methylpolysiloxane capillary column (13 m × 0.25 mm i.d., 0.25 μm film) using He (60 Kpa, 1 mL/min) as the carrier gas.

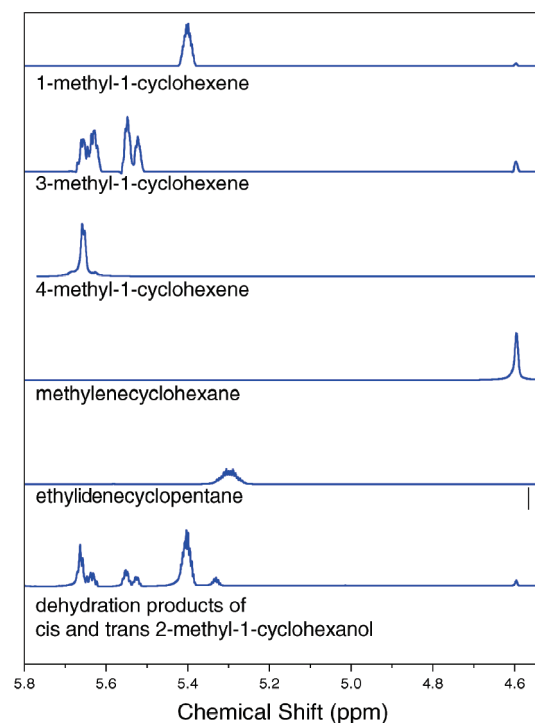
## HAZARDS

The methyl-1-cyclohexanols and methyl *tert*-butyl ether are combustible liquids and vapors. They may cause irritation to skin, eyes, and respiratory tract and may be harmful if swallowed or inhaled. Phosphoric acid is corrosive and contact can cause severe damage to skin and eyes. Chloroform may cause irritation to skin, eyes, and respiratory tract and may cause cancer if swallowed or inhaled.

## CLASS RESULTS

Two sets of data were obtained in the undergraduate organic chemistry laboratory experiment. One group of students generated data from the dehydration with direct distillation of products for *cis/trans*-2-methyl-1-cyclohexanol mixture. The other group of students carried out the same dehydration experiment with 10 min of reflux prior to distillation. In direct distillation, it has been proposed that the alkene products were volatilized quickly after they were formed.<sup>5</sup> If a dehydration–rehydration mechanism was occurring the product distribution from reflux prior to distillation would most likely be different than the direct distillation. For example, the refluxed reaction may be expected to yield an increased proportion of 1-methyl-1-cyclohexene, the most stable C<sub>7</sub>H<sub>12</sub> product. Analysis of reaction products was done by GC-FID, GC–MS, and <sup>1</sup>H qNMR.

Each student product was analyzed with GC-FID. Apparently, even with careful distillation, a portion of the original alcohol distills over with the water and alkene dehydration product. Therefore, the ratio of *cis/trans* starting alcohol residue in the distillate was measured along with the C<sub>7</sub>H<sub>12</sub> isomers. The results indicated that the ratio of *cis/trans*-2-methyl-1-cyclohexanol in the distillate was lower than the same ratio in the starting material. This may be due to the less stable alcohol being more rapidly dehydrated (Schemes 2 and 3). There was no significant difference between direct distillation and reflux followed by distillation of the dehydration products (Table 1). For the dehydration of 2-methyl-1-cyclohexanol, refluxing for 10 min before distillation did not appreciably change the ratio of 1-methyl-1-cyclohexene (83% without reflux vs 82% with reflux), 3- and 4-methyl-1-cyclohexene (14% without reflux vs 15% with reflux) and methylenecyclohexane (3% for both). It is important to note that 3- and 4-methyl-1-cyclohexene were not resolved



**Figure 1.** The quantitative proton nuclear magnetic resonance (qNMR) representation of the vinylic protons (4.5–5.8 ppm) of 1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, methylenecyclohexane, and ethylenecyclopentane compared to a dehydration product sample.

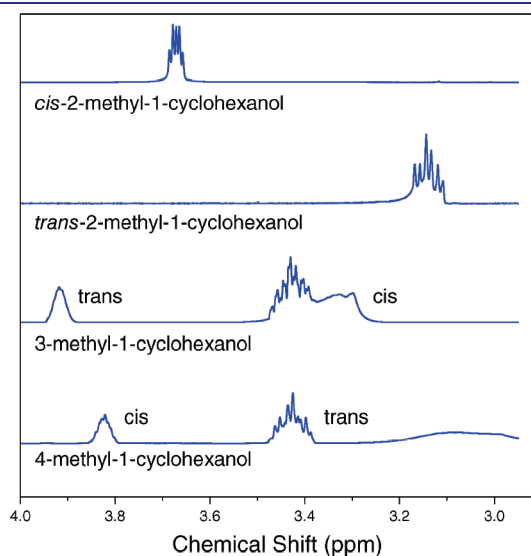
with GC. Nor have there been any reports that the two isomers can be separated by GC columns. This is a serious drawback to relying on GC for the analysis of dehydration products.

Because of the inherent inadequacies of the GC-FID analysis, selected student samples were analyzed with qNMR (400 MHz) and GC–MS methods. It is possible to distinguish between five commercially available C<sub>7</sub>H<sub>12</sub> isomers in <sup>1</sup>H NMR by the vinyl proton chemical shifts. In brief, the vinyl proton for 1-methyl-1-cyclohexene presents a signal at 5.42 ppm; the 2 vinyl proton signals for 3-methyl-1-cyclohexene were baseline separated and centered at 5.56 and 5.67 ppm. The splitting patterns of all the vinyl protons were complex due to the rigidity of the cyclohexene ring and long-range couplings. The two vinyl proton signals of 4-methyl-1-cyclohexene were overlapped in a complex signal centered on 5.69 ppm. The two vinyl protons of methylenecyclohexane form a singlet at 4.59 ppm. In addition, the vinyl proton of ethylenecyclopentane signal is centered at 5.33 ppm as shown in Figure 1. All dehydration products, 1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, methylenecyclohexane, and ethylenecyclopentane, were detectable in the qNMR spectrum in a ratio of 72.3, 15.7, 7.3, 1.2, and 3.5, respectively. Because the ratios, as determined by qNMR, are not dependant on detector response factors, they are more accurate than those measured by GC-FID.<sup>9</sup> It also must be noted that the reported GC-FID values were averages of student samples whereas the qNMR values were from single samples.

The ability to distinguish between 3- and 4-methyl-1-cyclohexene provides a significant improvement over the GC-FID method. Surprisingly, what is typically described as the 3-methyl-1-cyclohexene

product in 2-methyl-1-cyclohexanol dehydration is an approximately two-to-one mixture of 3- and 4-methyl-1-cyclohexanol, respectively. This evidence points to a deficiency in previous studies where the GC peak is interpreted as 3-methyl-1-cyclohexene. Proton NMR is also able to detect measurable quantities of what appears to be ethylenecyclopentane among the  $C_7H_{12}$  products. The reason why qNMR shows ethylenecyclopentane is present in three times the quantity of methylenecyclohexane when ethylenecyclopentane is not detectable by GC-FID may be explained by the overlap of ethylenecyclopentane and the 3-methyl-1-cyclohexene peak in the GC-FID experiment.

Figure 2 shows that it is also possible to distinguish between the *cis* and *trans* diastereomers of 2-, 3-, and 4-methyl-1-cyclohexanols by the chemical shift of the C1 (hydroxy methyne) hydrogens. The most stable diastereomer gives the upfield hydroxyl methyne signal for each isomer. For 2-methyl-1-cyclohexanols, the *cis* diastereomer has peaks centered at 3.68 ppm and *trans* diastereomer has peaks centered at 3.12 ppm. For 3-methyl-1-cyclohexanols, the *cis* diastereomer has peaks centered at 3.43 ppm and *trans* diastereomer at 3.92 ppm. For 4-methyl-1-cyclohexanols, the *cis* diastereomer has peaks centered at 3.82 ppm and *trans* diastereomer at 3.43 ppm. As can be seen from Figure 2, the only signals that significantly overlap are the C1 protons of *cis*-3-methyl-1-cyclohexanol and *trans*-4-methyl-1-cyclohexanol.

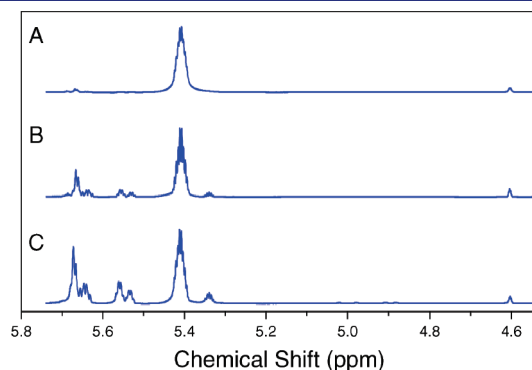


**Figure 2.** The quantitative proton nuclear magnetic resonance (qNMR) representation of the hydroxyl methyne (2.8–4.0 ppm) of *trans*-2-methyl-1-cyclohexanol, *cis*-2-methyl-1-cyclohexanol, *cis/trans*-3-methyl-1-cyclohexanol, and *cis/trans*-4-methyl-1-cyclohexanol.

## SPECIAL PROJECT RESULTS

As a result of the laboratory experiment, further investigation of the dehydration of 2-methyl-1-cyclohexanol was undertaken by a single student as a special project funded by an in-house undergraduate research grant. The laboratory course experiments were performed with commercial preparations of 2-methyl-1-cyclohexanol in which the two diastereomers are found in unequal quantities (*cis/trans* 1:2.6). As it has already been shown, the two diastereomers can be distinguished by GC and  $^1H$  NMR. Although it may seem problematic to use a mixture of diastereomers to reveal mechanistic information, it is also possible that interconversion between the two isomers occurs under the reaction conditions. To investigate the possible interconversion between the *cis*- and *trans*-2-methyl-1-cyclohexanol, *cis*-2-methyl-1-cyclohexanol was obtained and refluxed under mineral acid-catalyzed dehydration conditions. After 20 min, the reaction was extracted with methyl *tert*-butyl ether and analyzed for the presence of *trans*-2-methyl-1-cyclohexanol. No trace of *trans*-2-methyl-1-cyclohexanol was observed indicating that the interconversion between *cis*- and *trans*-2-methyl-1-cyclohexanol does not readily occur under these reaction conditions.

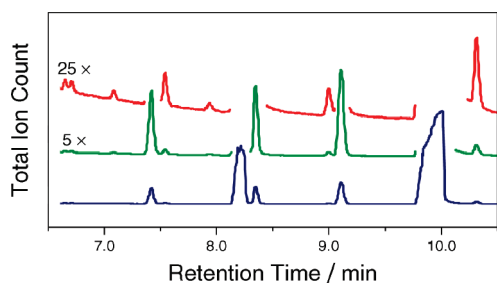
A further examination of the dehydration–rehydration hypothesis was investigated by refluxing 3-methyl-1-cyclohexene under mineral acid-catalyzed dehydration conditions. After 20 min, the reaction was extracted with methyl *tert*-butyl ether and analyzed for the presence of methylcyclohexanol. Proton qNMR showed no detectable alcohol formation. The qNMR trace did reveal the presence of 10% 1-methyl-1-cyclohexene that was not



**Figure 3.** The quantitative proton nuclear magnetic resonance (qNMR) analysis of the vinylic protons (4.5 to 5.8 ppm) of 1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, methylenecyclohexane, and ethylenecyclopentane obtained in the distillate of the acid-catalyzed dehydration experiment of (A) *cis*-2-methyl-1-cyclohexanol, (B) mixture of *cis* and *trans* isomers of 2-methyl-1-cyclohexanol, and (C) *trans*-2-methyl-1-cyclohexanol.

**Table 2.** The qNMR-Determined Products Obtained in the Distillate of Acid-Catalyzed 2-Methyl-1-cyclohexanol Dehydration Experiment

Starting Material	1-Methyl-1-cyclohexene (%)	3-Methyl-1-cyclohexene (%)	4-Methyl-1-cyclohexene (%)	Methylenecyclohexane (%)	Ethylenecyclopentane (%)
<i>cis</i> -2-Methyl-1-cyclohexanol	90.4	3.8	2.3	3.5	0
<i>cis/trans</i> -2-Methyl-1-cyclohexanol	79.6	7.7	8.2	1.6	3.0
<i>trans</i> -2-Methyl-1-cyclohexanol	60.5	19.6	11.2	1.0	7.7



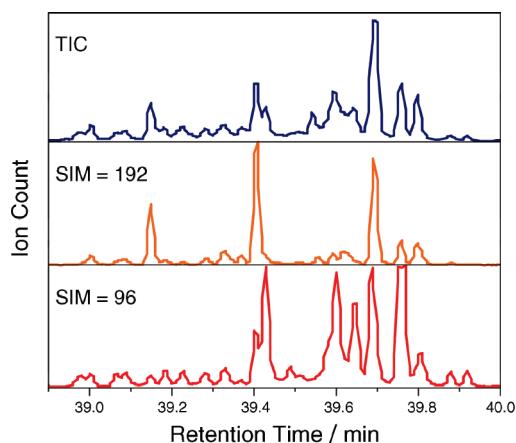
**Figure 4.** The GC–MS analysis of 1-methyl-1-cyclohexene (10.0 min), 3-methyl-1-cyclohexene (8.2 min), 4-methyl-1-cyclohexene (8.2 min), methylenecyclohexane (8.4 min), ethylidenecyclopentane (9.1 min), seven other  $m/z = 96$  components (6.5, 6.6, 7.1, 7.4, 7.5, 9.0, and 10.3 min) obtained from the dehydration of 2-methyl-1-cyclohexanol.

present in the starting material. Trace quantities of methylenecyclohexane (3.2%) and 4-methyl-1-cyclohexene (4.3%) were present in the starting material. No indication of rehydration of the alkene to an alcohol was observed. However, the presence of 1-methyl-1-cyclohexene does suggest that a small quantity of protonation–deprotonation occurred with the alkenes in refluxing aqueous acid solution.

Additional experiments were done with dehydrating the individual *cis* and *trans* isomers of 2-methyl-1-cyclohexanol under identical conditions. Table 2 shows that the dehydration of *cis*-2-methyl-1-cyclohexanol gives over 90% 1-methyl-1-cyclohexene and small quantities of 3-methyl-1-cyclohexene, methylenecyclohexane, and 4-methyl-1-cyclohexene. The dehydration of *trans*-2-methyl-1-cyclohexanol gives only 60% 1-methyl-1-cyclohexene with the remaining 40% divided between 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, ethylidenecyclopentane, and methylenecyclohexane. The dehydration of commercial *cis/trans*-2-methyl-1-cyclohexanol (with a 1:2.6 ratio of *cis* to *trans*) yields values that were in-between the *cis* and *trans* diastereomers as shown in Figure 3.

An earlier report, with results extrapolated from a mixture of diastereomers suggested that the *cis*-2-methyl-1-cyclohexanol produces 94% 1-methyl-1-cyclohexene and 6% 3-methyl-1-cyclohexene.<sup>5</sup> In contrast, this study indicated that appreciable quantities of both 4-methyl-1-cyclohexene and methylenecyclohexane were also produced from *cis*-2-methyl-1-cyclohexanol. The same report suggested that *trans*-2-methyl-1-cyclohexanol produces 75% 1-methyl-1-cyclohexene, 21% 3-methyl-1-cyclohexene, and 4% methylenecyclohexane. This study indicated that *trans*-2-methyl-1-cyclohexanol dehydration produces much less 1-methyl-1-cyclohexene (only 60.5%) and methylenecyclohexane (only 1%) whereas 4-methyl-1-cyclohexene and ethylidenecyclopentane were produced in significant quantities (11.2 and 7.7%).

GC–MS analysis of dehydration reactions gives a higher sensitivity perspective of the product distribution as shown in Figure 4. The dehydration of *trans*-2-methyl-1-cyclohexanol gives values for 1-methyl-1-cyclohexene, 3/4-methyl-1-cyclohexene (inseparable by GC), ethylidenecyclopentane, and methylenecyclohexane that were similar to qNMR. In addition, GC–MS detects seven more peaks with a  $m/z$  of 96 indicating a parent ion formula of  $C_7H_{12}$ . According to the National Institute of Standards and Technology (NIST) database, these peaks correspond to various  $C_7H_{12}$  isomers including 3,5-dimethylcyclopentene, methylethylidenecyclobutane, vinylcyclopentane, and 1-ethylcyclopentene. The definitive identification of these compounds



**Figure 5.** The GC–MS analysis (total ion count and single ion monitoring) obtained from the still pot extract after the dehydration of 2-methyl-1-cyclohexanol reaction was complete.

could not be made as standards were not commercially available. What is more, GC–MS also indicates the presence of cyclohexene ( $m/z = 82$  at 5.9 min), ethylcyclopentane ( $m/z = 98$  at 7.9 min), and toluene ( $m/z = 92$  at 9.7 min).

In addition to the  $C_7H_{12}$  products, dimeric  $C_{14}$  products were observed in GC–MS of the still pot extract of the dehydration reaction. Single ion monitoring (SIM) of the MS chromatogram indicates that  $C_{14}H_{24}$  structures were present in cluster of peaks between 38.9 and 40 min as shown in Figure 5.

## CONCLUSION

The prediction explored here was the possibility that an equilibrium between dehydration and hydration played a significant role in the product distribution (Scheme 6) of the phosphoric acid-catalyzed dehydration of 2-methyl-1-cyclohexanol. The modification was made by refluxing the reaction mixture before distilling off the alkene products. Students perceived that the reaction was not appreciably reversible under the reaction conditions. The presence of products that cannot be explained by either the E1 or E2 mechanisms found in the textbook presented a challenge to organic chemistry students. The students had to go beyond the textbook explanations of elimination mechanisms to address this question. To that end, students were given access to scientific articles that discuss similar mechanistic problems if they choose to investigate this problem further.

## ASSOCIATED CONTENT

### Supporting Information

Student handout and prelab assignment. This material is available via the Internet at <http://pubs.acs.org>.

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