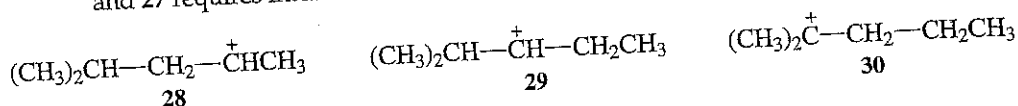
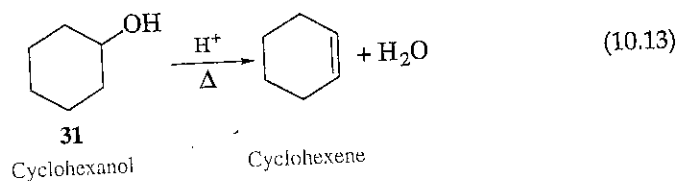


including 4-methyl-1-pentene (23), *trans*-4-methyl-2-pentene (24), *cis*-4-methyl-2-pentene (25), 2-methyl-2-pentene (26), and 2-methyl-1-pentene (27). A pathway to 23–25 involves deprotonating the intermediate carbocation 28. However, forming 26 and 27 requires intervention of carbocations 29 and 30 (see Exercise 13).



In contrast to 22, cyclohexanol (31) undergoes acid-catalyzed dehydration *without* rearrangement to yield a single product (Eq. 10.13). This reaction may be accompanied by acid-catalyzed polymerization of the desired cyclohexene, however.



EXPERIMENTAL PROCEDURES

Dehydration of Alcohols



Discovery Experiment

Purpose To determine the product distribution in the acid-catalyzed dehydration of alcohols to alkenes.

SAFETY ALERT



1. Wear safety glasses or goggles and suitable protective gloves while performing the experiments.
2. The majority of materials, particularly the product alkenes, that will be handled during this experiment are highly flammable, so use *flameless* heating and be certain that there are no open flames in your vicinity.
3. Several experimental operations require pouring, transferring, and weighing chemicals and reagents that cause burns on contact with your skin. Should acidic solutions accidentally come in contact with your skin, immediately flood the affected area with water, then wash it with 5% sodium bicarbonate solution.

A ■ Dehydration of 4-Methyl-2-Pentanol

MINISCALE PROCEDURE

Preparation Refer to the online resources to answer Pre-Lab Exercises, access videos, and read the MSDSs for the chemicals used or produced in this procedure. Review Sections 2.4, 2.9, 2.10, 2.11, 2.13, 2.14, 2.22, 2.25, 2.27, and 6.4.

Apparatus A 25-mL and two 10-mL round-bottom flasks, drying tube, ice-water bath, apparatus for simple and fractional distillation, magnetic stirring, and *flameless* heating.

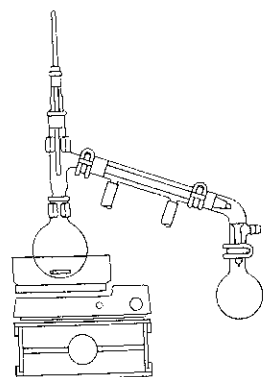
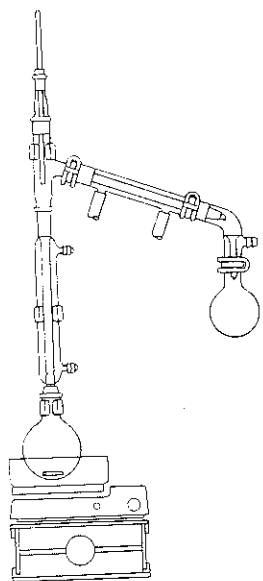
Setting Up Place a stirbar and 4.0 mL of 4-methyl-2-pentanol in the 25-mL round-bottom flask. Add 2.5 mL of 9 M sulfuric acid and thoroughly mix the liquids by gently swirling the flask. Equip the flask for fractional distillation and use an ice-water bath to cool the receiving flask.

Elimination Heat the reaction mixture and collect all distillates while maintaining the head temperature below 90 °C. If the reaction mixture is not heated too strongly, the head temperature will stay below 80 °C for most of the reaction. When about 2.5 mL of liquid remains in the reaction flask, discontinue heating. Transfer the distillate to an Erlenmeyer flask and add several spatula-tips full of *anhydrous* potassium carbonate to neutralize any acid and to dry the distillate.★ Occasionally swirl the mixture during a period of 10–15 min to hasten drying; add additional portions of *anhydrous* potassium carbonate if the liquid remains cloudy.

Isolation Transfer all of the dried organic mixture into a dry 10-mL round-bottom flask by decantation or by using a Pasteur pipet. Add a stirbar and equip the flask for simple distillation (Fig. 2.37a). Use a tared 10-mL flask as the receiver. Protect the receiver from atmospheric moisture by equipping the vacuum adapter with a drying tube and cool the receiver in an ice-water bath.

Isolate the alkenes by simple distillation. The expected products of the reaction are 4-methyl-1-pentene, *cis*-4-methyl-2-pentene, *trans*-4-methyl-2-pentene, 2-methyl-1-pentene, and 2-methyl-2-pentene. Collect the fraction boiling between 53 °C and 69 °C (760 torr) in a pre-weighed, dry 10-mL receiving flask.

Analysis Weigh the distillate and determine the yield of products. Test the distillate for unsaturation using the bromine and Baeyer tests (Secs. 4.7A1 and 4.7A2, respectively). Analyze your distillate by GLC or submit a sample of it for analysis. After obtaining the results, calculate the relative percentages of the isomeric alkenes formed; assume that the response factors are identical for the isomers. A typical GLC trace of the alkenes from this elimination is shown in Figure 10.10. Obtain IR and NMR spectra of your starting material and compare your spectra with those of an authentic sample (Figs. 10.11 and 10.12).



B • Dehydration of Cyclohexanol

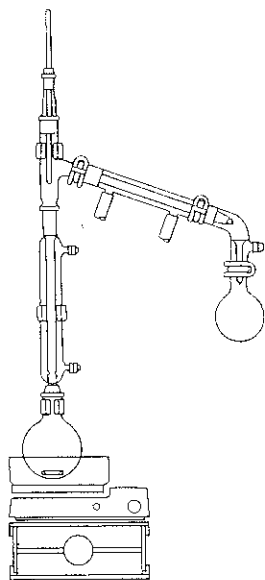
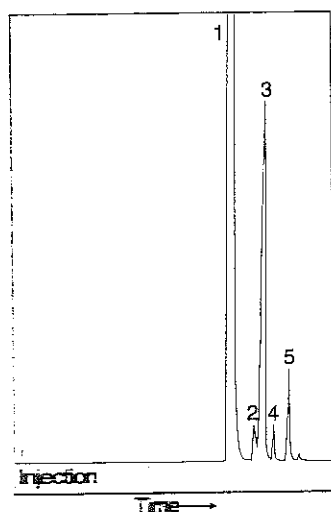
MINISCALE PROCEDURE

Preparation Refer to the online resources to answer Pre-Lab Exercises, access videos, and read the MSDSs for the chemicals used or produced in this procedure. Review Sections 2.9, 2.10, 2.11, 2.13, 2.14, 2.22, 2.27, and 6.4.

Apparatus A 25-mL and two 10-mL round-bottom flasks, drying tube, ice-water bath, apparatus for simple and fractional distillation, magnetic stirring, and *flameless* heating.

Figure 10.10

GLC trace of the product mixture from the dehydration of 4-methyl-2-pentanol. Assignments and peak areas (in parentheses): peak 1: diethyl ether (solvent for analysis); peak 2: 4-methyl-1-pentene (3030); peak 3: cis- and trans-4-methyl-2-pentene (51693); peak 4: 2-methyl-1-pentene (228); peak 5: 2-methyl-2-pentene (9733). Column and conditions: 0.25-mm \times 30-m APT-Hex; 37 °C, 35 mL/min.



Setting Up Place a stirbar and 5.0 mL of cyclohexanol in the 25-mL round-bottom flask. Add 2.5 mL of 9 M sulfuric acid and thoroughly mix the liquids by gently swirling the flask. Equip the flask for fractional distillation and use an ice-water bath to cool the receiving flask.

Elimination and Isolation Follow the same protocol as provided in Part A, with the *single exception* that the product should be collected over the range of 80–85 °C (760 torr). Note that water and cyclohexene form a **minimum-boiling azeotrope**, which is a mixture of the two compounds that distills *below* the boiling point of either pure compound (see Figure 10.4). This makes it vital that the crude product be dried *thoroughly* prior to the simple distillation.

Analysis Weigh the distillate and, assuming that it is pure cyclohexene, determine the yield of product. Test the distillate for unsaturation using the bromine and Baeyer tests (Secs. 4.7A1 and 4.7A2, respectively). Analyze your distillate by GLC or submit a sample of it for analysis. Obtain IR and ^1H NMR spectra of your starting material and product and compare them with those of authentic samples (Figs. 10.23–10.26).

MICROSCALE PROCEDURE

Preparation Refer to the online resources to answer Pre-Lab Exercises, access videos, and read the MSDSs for the chemicals used or produced in this procedure.
Review Sections 2.4, 2.9, 2.13, 2.22, 2.25, and 6.4.

Apparatus A 3-mL conical vial, apparatus for magnetic stirring, simple distillation, and *flameless* heating.

Setting Up Place a spinvane in the conical vial. Using a calibrated Pasteur pipet, add 1 mL of cyclohexanol and 0.5 mL of 9 M sulfuric acid to the vial. Thoroughly mix the contents by briefly stirring or swirling the liquid for a few seconds. Equip the vial for microscale distillation and circulate cold water through the condenser.