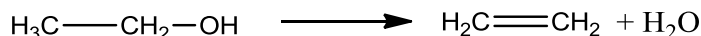


Reminder: These notes are meant to supplement, not replace, the lab manual.

Dehydration of 2-methylcyclohexanol

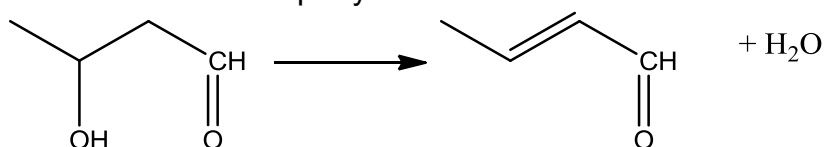
History and Application:

Alcohols are readily dehydrated to alkenes by using an acid catalystⁱ. In Brazil, where ethanol is a readily available, ethylene is made by a dehydration route.



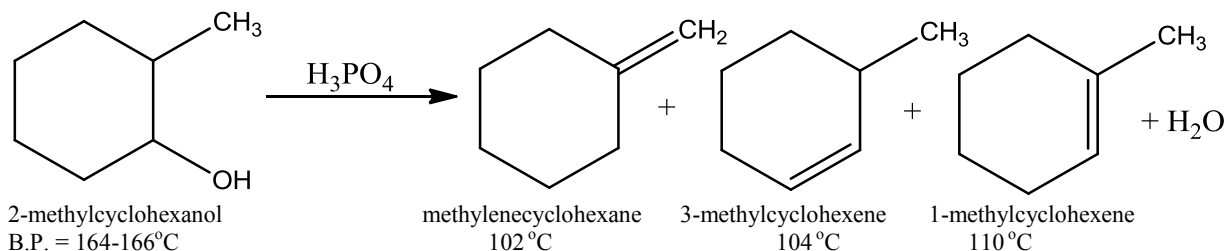
The ethylene is then made into the plastic polyethylene. In this way the plastic is made not from petroleum products as is common in the rest of the world, but instead is made from grain.ⁱⁱ

Another common alcohol dehydration is the transformation of acetaldol (2-hydroxy butanal) into crotonaldehyde (2-butenal). Crotonaldehyde is used in the manufacture of sorbic acid which is a widely used food preservative. (Read the ingredients on your snack bags). This process is used to make approximately 25,000 tonnes of sorbic acid per yearⁱⁱⁱ.



The Experiment

An alcohol is dehydrated and an alkene is formed. In today's experiment, 2-methylcyclohexanol is reacted with phosphoric acid, and three different products can result. The overall reaction is shown below.

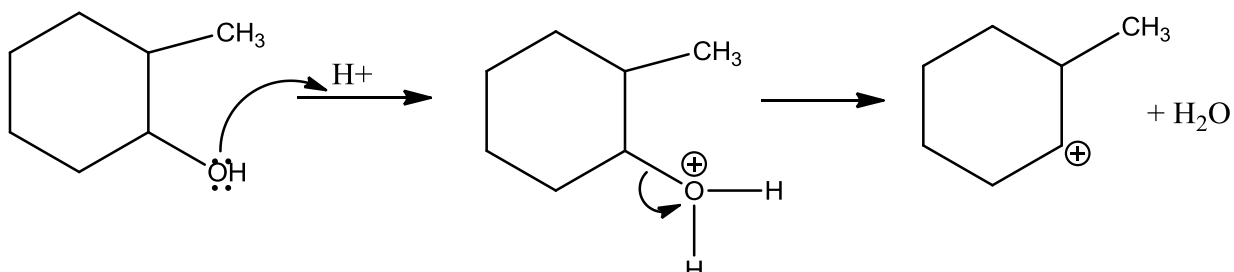


This means that any single molecule of 2-methylcyclohexanol can form into 3-methylcyclohexene, 1-methylcyclohexene or methylenecyclohexane. One molecule cannot form 3 molecules. Which product alkene do you predict to be the most stable? (Remember Zaitsev's rule.)

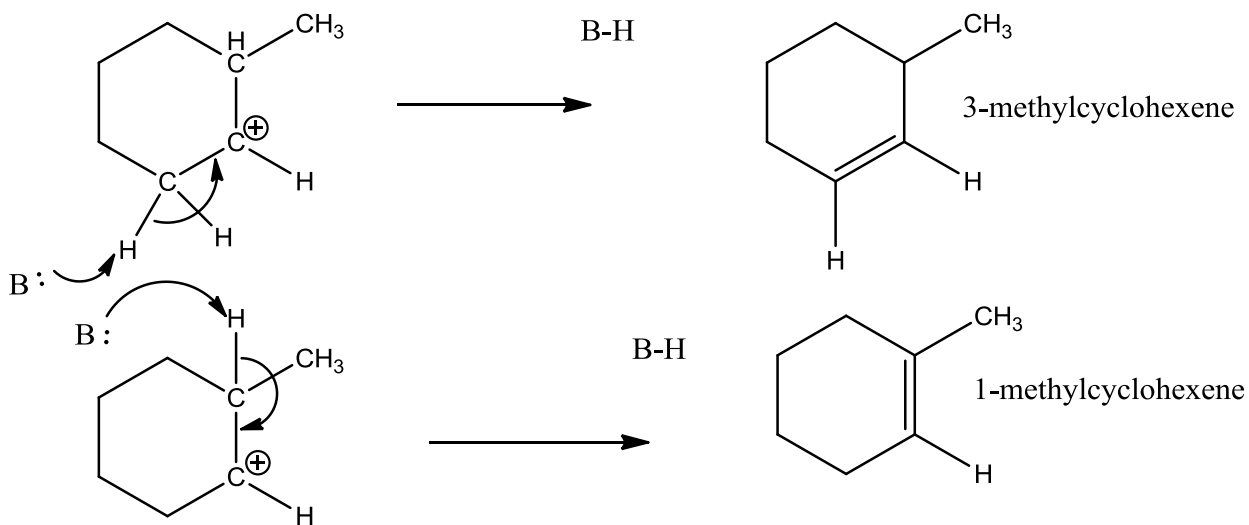
The phosphoric acid acts as a catalyst. Phosphoric acid protonates the alcohol group and turns the poor leaving group (-OH) into a very good leaving group (-OH₂⁺). The departure of the leaving group forms a 2° carbocation. This carbocation can form two of the products with the elimination of a H on an adjacent carbon, 1-methylcyclohexene and 3-methylcyclohexene. Alternatively the 2° carbocation can undergo a rearrangement forming a more stable 3° carbocation. This carbocation can form two products methylenecyclohexane and 1-methylcyclohexene. The product distribution can be under either kinetic or

thermodynamic control. Typically the conditions in this lab favor thermodynamic control. The full mechanism follows.

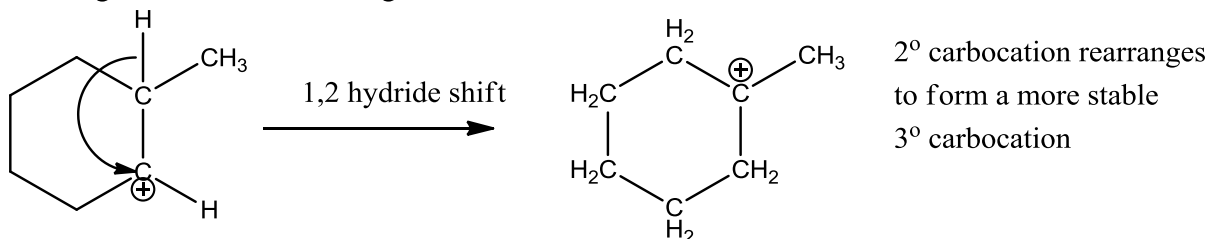
The dehydration of 2-methylcyclohexanol begins with the protonation of the -OH by the acid, transforming it from a poor leaving group to a good leaving group. This group leaves as a water molecule, forming a 2° carbocation.



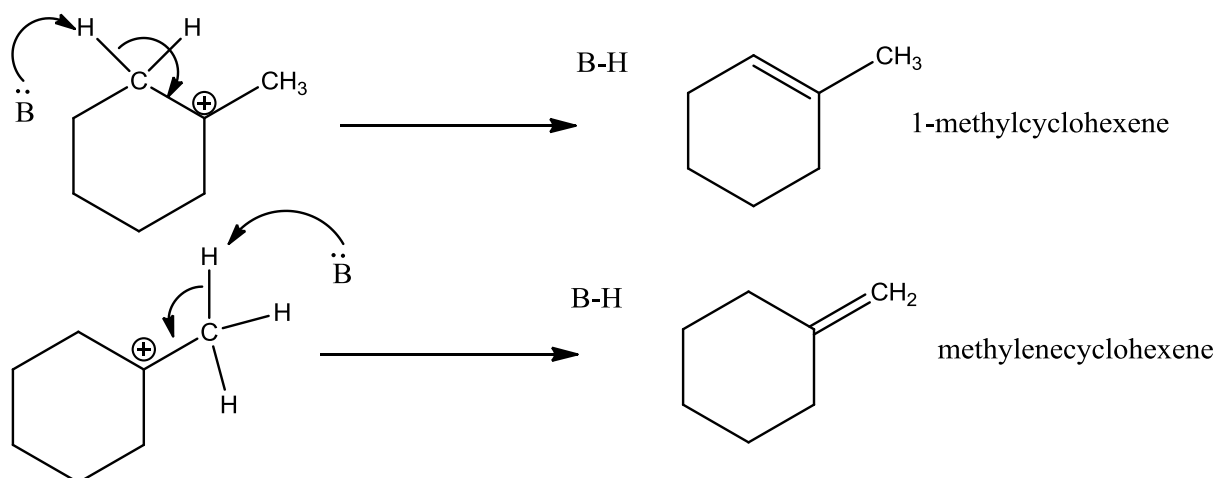
This carbocation can undergo direct elimination to form 2 possible products...



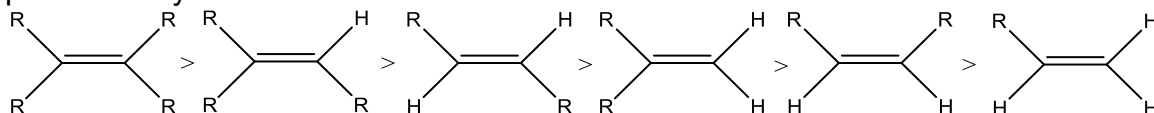
...or undergo a carbocation rearrangement to form a new carbocation.



This new carbocation can undergo elimination to form 2 products (one is the same as from above)



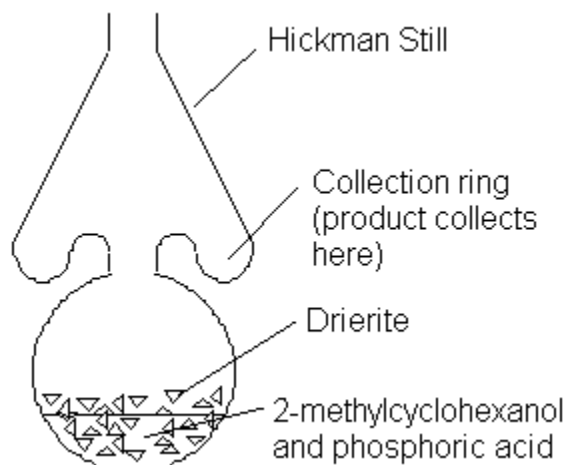
Alkenes with the highest degree of substitution are the lowest energy and most stable. Typically (Zaitsev's Rule) the most energetically favored is formed preferentially.



Knowing this, which of the three products is predicted to be present in the largest amount?

Procedure

The reaction will be carried out in a Hickman still. These are custom manufactured pieces of glassware. The Drierite, phosphoric acid, and 2-methylcyclohexanol are contained in the bottom portion of the still.



Only the lower 1/3 of the still bottom should be buried in the sand. Some Drierite should be above the level of the sand. The Drierite will absorb the water from the 85% phosphoric acid and absorb the water that is liberated during the dehydration. The Drierite also acts as a boiling stone and a fractionation column. The temperature of the sand should not be allowed to rise above the boiling point

of the 2-methylcyclohexanol. As the products form, they will vaporize (boiling points 102-110°C), and rise in the still. They will condense on the glass in the upper portion of the still and run down the glass, collecting in the ring. Why doesn't the starting material also vaporize, condense and collect in the ring?

Analysis

The starting alcohol and product will be analyzed using IR. The IR of 2-methylcyclohexanol will have a distinct OH stretching absorbance near 3400cm^{-1} . This peak is absent from the IR spectrum of the alkene products. The IR spectrum of the product contains a sp^2 stretch around 3050cm^{-1} . This peak is not always clear. A C=C stretch may also be observed around 1600cm^{-1} . Water present in the product will show a typical absorbance in the 3400cm^{-1} region and will be difficult to distinguish from the alcohol stretch.

Safety

Phosphoric acid is highly corrosive. Wear eye protection the entire time in lab when anyone is working. Clean up all spills immediately. Never look directly down the barrel of a heating still.

All of the organic materials are highly flammable and slightly toxic. Keep away from direct flames. The alkene products have a strong noxious odor. Keep products capped or in the hood to reduce vapor.

Hot sand baths look cool.

Unplug sand baths when finished heating.

References

ⁱ Weissermel, K, Arpe, H.-J., *Industrial Organic Chemistry, 3rd Completely Revised Edition*, VCH, New York, 1997 p185

Heaton, A., *An Introduction to Industrial Chemistry, 3rd*, Blackie Academic and Professional, London, 1996
Chenier, P.J., *Survey of Industrial Chemistry, 3rd*, Kluwer Academic, New York, 2002

ⁱⁱ <http://www.icis.com/Articles/2009/07/15/9232844/Brazilian-ethanol-attracts-bioplastics-investors.html> (January 28, 2010)

ⁱⁱⁱ <http://www.scidesign.com/> September 10, 2009
http://pcinylon.com/pci/details.php?catp=50000000&p_id=4&ojid=8e922196f389c06ef0b2d0810c555145
September 17, 2009

^{iv} D. Klein, *Organic Chemistry*, Wiley, New York, 2012, p344