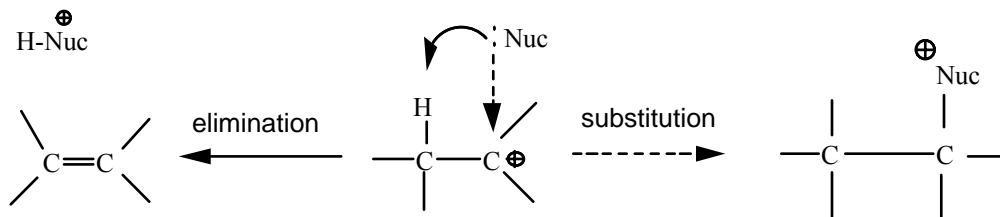


CHEM 321: AN E1 REACTION: CYCLOHEXENE FROM CYCLOHEXANOL

Elimination always competes with substitution. This is because any nucleophile is also a base on account of its (relatively) rich electron supply. Since a base is present, abstraction of a hydrogen ion is a possibility instead of attack at the electron-deficient carbon atom:

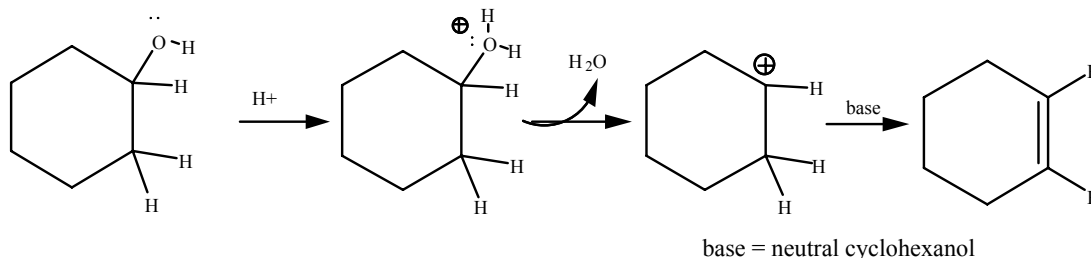


Substitution is the favored process at low temperature, but elimination predominates if the reaction temperature is high. Just as with substitution, there are two elimination pathways: E1 and E2. In the unimolecular pathway, substitution and elimination share the same slow step: a carbocation intermediate must form. This means that the **rate at which substrate is consumed** is fixed regardless of what product (elimination or substitution) forms. However, the **predominant product** of a particular unimolecular reaction depends on what happens after the slow step. In this experiment, the temperature is high, and elimination predominates. Strong acid is added in order to change the alcohol's poor leaving group ($-\text{OH}$) into a good leaving group (water) so as to favor a carbocation intermediate. Phosphoric acid is used instead of other common strong acids for two major reasons:

(a) the anion of phosphoric acid (H_2PO_4^-) is a poor nucleophile, so the tendency toward substitution is minimized, favoring elimination; and

(b) sulfuric acid, normally a logical choice as a strong acid, favors polymerization and degradation of the alcohol.

The elimination reaction is shown below.



Carbocations are extremely reactive, so other products should be expected. The cation might be attacked by the oxygen of an unprotonated cyclohexanol, forming dicyclohexyl ether. Or, the π -cloud of cyclohexene might attack the cation, leading to a dicyclohexyl cation which could form a larger (polymeric) alkene upon loss of a proton. Normally, one should consider the possibility of rearrangement. Unsubstituted cyclohexyl cations don't rearrange since no cation of greater stability can form.

EXPERIMENTAL SECTION → Partners!

CAUTION: *Phosphoric acid is a strong acid that can cause serious skin burns and damage clothing. Immediately wipe up any spills and wash skin or clothing with lots of water followed by a little sodium bicarbonate solution, then a final rinse with more water.*

CAUTION: *Cyclohexene is a skin irritant. Avoid skin contact. It is also volatile and very flammable. Don't breathe its vapors. Watch out for ignition sources in its vicinity.*

[In the protocol that follows, the reacting mixture is heated not only to favor elimination but also to drive off the more volatile alkene and water that results from the elimination as it forms, an application of Le Châtelier's principle, and to minimize side reactions. Why does the alkene have a significantly lower boiling point than the parent alcohol?]

Weigh cyclohexanol (20 g, may need to be melted) into a tared 100 mL boiling flask and add a boiling chip. Add about 6 mL of 85% phosphoric acid. Assemble apparatus for simple distillation with a 50 mL receiving flask. After you are sure the thermometer is properly positioned, insulate the upper part of the boiling flask and distilling head. Heat the mixture at a gentle boil, making sure the vapor temperature does not exceed 100° C. If the vapor temperature rises too high, unreacted cyclohexanol will distill over. You must be rather patient. The reaction is fairly slow, and you just have to wait while the alkene forms. The distillate (the liquid that collects in the receiving flask) will have a cloudy layer on top and a clear layer below. The reaction is over when the liquid remaining in the boiling flask becomes cloudy, viscous, and slightly yellow.

Pour the distillate from the receiving flask into a 125 mL separatory funnel and discard the lower layer. Wash the organic layer with 10-15 mL of 5% sodium bicarbonate solution to neutralize any acid that may have been entrained in the vapor stream during distillation. Decant the product carefully into a dry 50 mL Erlenmeyer flask and rid it of visible water. Dry it with a little anhydrous CaCl₂ by swirling the stoppered flask slowly for about 10 minutes. Use a Pasteur pipette to transfer the liquid into a dry 50 mL boiling flask (if the organic layer got cloudy from the CaCl₂ dust particles, remove those by gravity filtration), add a boiling chip, and distill through dry glassware into a dry pre-weighed 25 mL receiving flask. Record the temperature when 1) the first drop drips into the receiving flask, 2) there is a constant drip rate into the receiving flask, and 3) the drip rate slows down. What is the accepted boiling range of the desired product? Keep this range in mind as you distill over the product. If you distill too much beyond the boiling range of the desired product, it will be contaminated with the side product. If the distillate appears cloudy, then dry it over about 10-15 pellets of anhydrous CaCl₂, swirl it until clear, and decant the liquid into a preweighed, dry, glassware. Record the mass of product.

ANALYSIS

Think of two chemical tests to characterize the structure of the product and perform them along with positive and negative controls (*name the chemicals used!*). Each test should require only 1-2 drops of product.

Run an IR spectrum of your product using the ATR accessory of the IR instrument. Work rapidly because the product evaporates fast.

CLEAN UP

Boiling flask residues go down the drain. Pour your product into the "student prep cyclohexene" bottle.

REPORT

As always, include only essential experimental information and assure that the Results/Discussion addresses the objectives of the experiment. Avoid BS!!

Up until now, you have had the experimental objectives stated for you. In this lab report AND in each subsequent lab report, it is up to you to use your scientific knowledge to generate the objectives. In proposing these objectives for this lab report, here are some things to consider:

1. What reaction mechanism did we wish to favor in this experiment? Is there any mechanism that is in competition with the desired reaction mechanism? If so, what is it, and how did the experimental design mostly avoid this competing reaction?
2. What chemical principle was exploited to "push" or "pull" the desired reaction towards the products? Why was it important to maintain the vapor temperature below 100 °C during the reaction? What was the purpose for using a dilute NaHCO₃ solution?
3. What two methods were employed to characterize the product?

NOTE: These questions should not appear in your lab report. They are designed to help you think critically as you formulate the objectives as part of a complete introduction.