



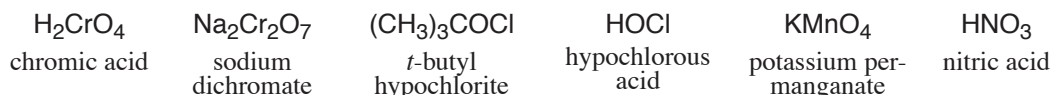
## Experiment 3

### Oxidation of Alcohols: Preparation of Cyclohexanone

**Reading:** *Organic Chemistry* by Francis Carey, 5<sup>th</sup> edition, pp. 87-90 (2.19); pp. 641-645 (15.10).

**Technique:** Extraction.

Compounds containing the ketone or aldehyde functional group are important in organic chemistry. They are common in nature and are often key intermediates in organic synthesis. Useful methods for preparation of ketones include the coupling of acid chlorides with organocopper reagents and the hydration of alkynes. Aldehydes can be prepared by reduction of acid chlorides with certain metal hydrides or by catalytic hydrogenation. However, the most important method for preparation of both ketones and aldehydes is the oxidation of alcohols. Alcohols are among the most readily available organic compounds, and therefore, this method for preparation of aldehydes and ketones is extremely useful.



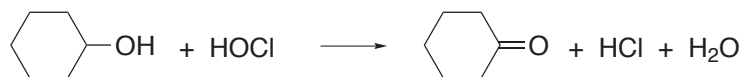
Primary and secondary alcohols are oxidized to the corresponding aldehydes and ketones by various oxidizing agents, e.g., dichromates, *t*-butyl hypochlorite, hypochlorous acid, potassium permanganate, and nitric acid. The aldehydes derived from primary alcohols can be further oxidized to carboxylic acids by some of these oxidizing agents (including HOCl), while the ketones derived from secondary alcohols are stable to further oxidation.

The most widely used oxidizing agent is chromic acid, which is prepared by mixing sodium dichromate with sulfuric acid. However, chromium salts are suspected mutagens and carcinogens, and strict EPA regulations exist for the handling and disposal of chromium compounds.

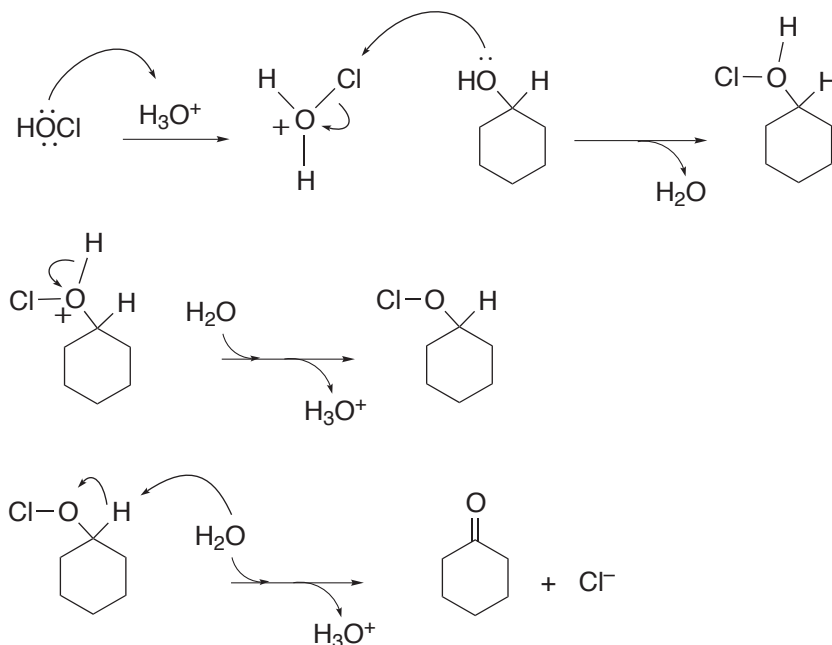
Hypochlorous acid (HOCl), an alternative oxidizing agent, is readily available, inexpensive, safe, and environmentally sound as compared to the dichromates. Although HOCl is unstable and decomposes slowly to upon storage, it can be prepared from a common household item: bleach. Household bleach contains sodium hypochlorite which, when treated with acetic acid, produces the active oxidizing agent:



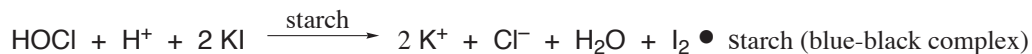
In this experiment, a mixture of bleach and acetic acid will be used to prepare cyclohexanone from cyclohexanol (Chapman-Stevens Oxidation).



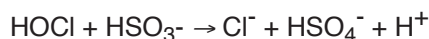
The mechanism for this reaction has not been fully established, although the following seems likely:



In order for the reaction of hypochlorous acid and cyclohexanol to go to completion, the hypochlorous acid must be in excess during the reaction. Since the concentration of hypochlorite in household bleach varies, the presence of excess hypochlorous acid cannot be assumed by adding an excess based on the molar amount of cyclohexanol and assuming household bleach to be 5.25% sodium hypochlorite. Instead, the presence of hypochlorous acid must be established by a chemical test, the potassium iodide-starch test. This test employs paper impregnated with iodide ions and starch (KI-starch test paper); a drop of the reaction mixture is placed on the paper. If hypochlorous acid is present, it oxidizes the iodide ion in the test paper to iodine, which in turn forms a blue-black complex with the starch in the test paper:



At the end of the reaction period, any excess oxidizing agent must be destroyed. This is accomplished by the addition of sodium bisulfite ( $\text{NaHSO}_3$ ) which reduces excess oxidant according to the equation below:



To determine if enough bisulfite has been added, the reaction mixture is again tested with KI-starch test paper, this time, the *absence* of hypochlorous acid is the desired result.

After neutralization with sodium hydroxide, the cyclohexanone is “salted out” by adding solid  $\text{NaCl}$ . Salting out is a common organic chemistry practice, based on the

principle that dissolved inorganic salts decrease the solubility of most organic compounds in water. The cyclohexanone is extracted into methylene chloride and the resulting solution treated with drying agent and heated to evaporate off the methylene chloride. High purity cyclohexanone could then be obtained by distilling the product, a method which would also help to identify the product by giving the boiling point. You will not have time to distill the product. Instead, you will run an IR of your product. The IR will indicate both the identity and the purity of your cyclohexanone.

### Safety Precautions

Concentrated acetic acid, sodium hypochlorite, and sodium bisulfite are corrosive to the skin. If you get any of these reagents on you, wash the affected area well with water. While methylene chloride is rated as only a moderate health hazard, you should still avoid contact with this reagent. Wear gloves and protective clothing. Sodium carbonate, cyclohexanol, and cyclohexanone are irritants—avoid skin contact.

### Procedure Section

Place 10 mmoles of cyclohexanol and a stir bar in an Erlenmeyer flask. Place over a stir motor and stir while you carefully add 2.5 mL of acetic acid (conc.). Place 15 mL of bleach (approximately 5.25% sodium hypochlorite<sup>\*</sup>) in your separatory funnel, position the separatory funnel above the Erlenmeyer flask, and add the bleach dropwise to the cyclohexanol/acetic acid mixture. The addition of bleach should take about 15 min. If the reaction flask becomes hot to the touch during the bleach addition, use an ice bath to cool it down. When the addition of the bleach is complete, the solution will be pale yellow to yellow-green in color. Test the solution for excess hypochlorous acid and, if necessary, add additional bleach.

Stir the reaction mixture for an additional 15 min at room temperature. Then, quench excess oxidant by adding about 0.5 mL of saturated sodium bisulfite solution.<sup>†</sup> Test for excess hypochlorous acid and, if necessary, add additional sodium bisulfite.

Add 2 drops of thymol blue (an indicator), then add 6N NaOH until the solution is just basic. Add solid NaCl until the solution is saturated with salt, then decant the liquid into your separatory funnel. Extract with 5 mL of methylene chloride, save the organic layer, then extract the aqueous layer one more time with 5 mL of methylene chloride.

**Caution:** if the aqueous layer is warm, a lot of pressure can build up in the separatory funnel when it is shaken with methylene chloride. Be sure to vent your separatory funnel frequently during the extraction.

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\* Sodium hypochlorite (NaOCl) is available only in solution. A 5.25% aqueous solution is 5.25 grams of NaOCl in a total volume of 100 mL.

† Saturated sodium bisulfite is approximately 30 grams of sodium bisulfite in 100 mL of water.

Combine the organic layers and dry over anhydrous sodium sulfate. Filter or decant to remove the drying agent. Remove the methylene chloride from the solution either by evaporating it on a steam bath (do not forget to add a boiling chip!) or by placing it in a side arm flask, stoppering it, and applying vacuum until bubbling is no longer apparent.

Determine your yield and run an IR of the product.

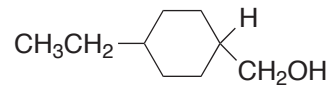
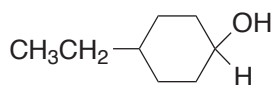
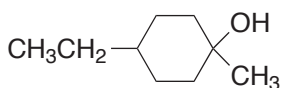
### Wastes

*Aqueous Waste:* The aqueous layer remaining after methylene chloride extraction and the test reagents.

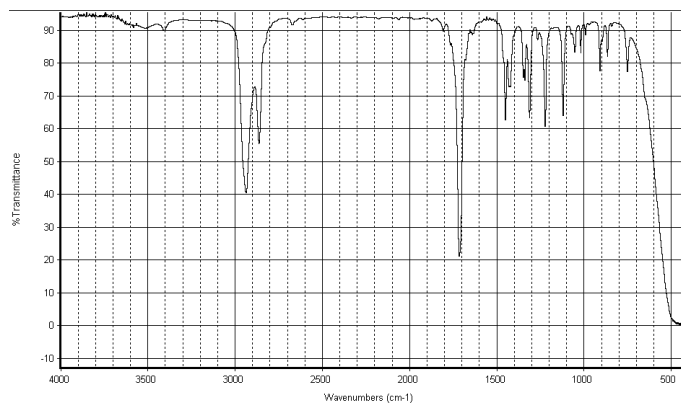
*Recovery Jar:* For the product, cyclohexanone.

### Study Questions

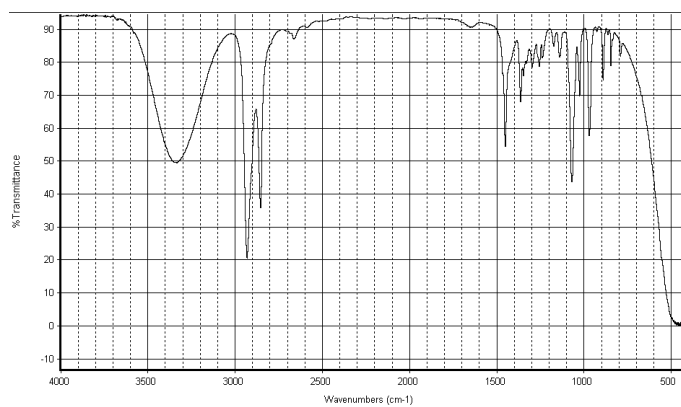
- 1) If a procedure requires 10.0 g of HOCl, how many mL of 20% (aq.) NaOCl are needed? (*Hint:* see the footnote in the Procedure section which defines “%” solutions.)
- 2) Show the product that results when hypochlorous acid (HOCl) oxidizes each compound below. If no reaction occurs, write “No Reaction.”



- 3) The IR spectra of cyclohexanol and cyclohexanone are given in Figure 3.1. Identify which spectrum belongs to which compound and assign the bands in each spectrum to substantiate your choice.



Spectrum A



Spectrum B

Figure 3.1 The spectra of cyclohexanol and cyclohexanone. Which is which?

