1. Glacial acetic acid can cause severe burns. Do not get it on your skin, clothing or in your eyes. Transfer this material in the hood only. If any contacts your skin or eyes, flush the exposed area for at least fifteen minutes with cold water.

2. Chlorine gas is a respiratory and eye irritant. Some chlorine gas is produced when bleach is added to acetic acid. Therefore, carry out this process in the hood and/or with an apparatus connected to a vacuum line.

3. From the label of a bottle of bleach: "Causes substantial but temporary eye injury. Do not get in eyes or in clothing. Harmful if swallowed. May irritate skin. Wash thoroughly with soap and water after handling." Also, keep chlorine bleach in stoppered containers so that the lab does not fill up with chlorine gas.

4. 6M NaOH is caustic. Exercise care in its use. If spilled on skin rinse for fifteen minutes with cold water.

5. Cyclohexanol, cyclohexanone, and ethanol are all to some degree toxic and irritating. Handle these chemicals in the hood. If any area of your person comes in contact with these chemicals, flush the exposed area for at least fifteen minutes with cold water. These chemicals are also flammable. Flames are never allowed in the lab.

6. The chromic acid and 2,4-dinitrophenylhydrazine solutions are extremely corrosive. Chromic acid is also highly toxic. Wear two pairs of gloves and your goggles when working with these chemicals. Work in the hood and do not take any more chemical than you need. For your information, like all organics, the 2,4-DNP solution is irritating and flammable. Both of these solutions stain everything they come in contact with. Be especially careful not to spill them.

7. Generally, WEAR GLOVES AND GOGGLES. WORK IN THE HOODS. ALERT YOUR INSTRUCTOR/TA AS TO ANY CHEMICAL EXPOSURE OR LARGE SPILLS OF MATERIALS. CONSULT YOUR INSTRUCTOR/TA REGARDING THE DISPOSAL OF WASTE.
<table>
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<td><strong>TOTAL</strong></td>
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<td>(percent)</td>
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This is your report cover. Please fill this out and attach it to the appropriate prelab pages of the form that follows the text of this lab. Please note: This is a form write-up!!!!! All that should be completed and turned in are the forms.
Experiment 9a
Flow Chart

cyclohexanol

1. add glacial acetic acid
2. slowly add bleach
3. stir for 20 minutes
4. starch-iodide test
5. add sodium bisulfite soln.
6. Neutralize with 6M NaOH
7. simple distillation, steam distillation

pot residue distillate

discard water + cyclohexanone + cyclohexanol

1. saturate with NaCl
2. extract

aqueous organic

discard cyclohexanone + water + cyclohexanol

1. add mag. sulfate (anh)
2. filter through glass wool

residue filtrate

discard cyclohexanone + cyclohexanol
Experiment 9
Oxidation:
Oxidation of Cyclohexanol to
Cyclohexanone Using Household Bleach

Background

Although both Cr (VI) compounds (e.g. H₂CrO₄) and KMnO₄ have been widely used for oxidizing alcohols to carbonyl compounds, each has its disadvantages. Chemists also use various reagents containing chlorine in a positive oxidation state. Examples include tert-butyl hypochlorite, (CH₃)₃OCl, and chlorine complexed to various reagents. Another useful reagent for this purpose is sodium hypochlorite, NaOCl, the active ingredient in household bleach. The hypochlorite ion, OCl⁻, contains chlorine in the +1 oxidation state.

You are to follow the procedure given below for the oxidation of cyclohexanol to cyclohexanone using household bleach. This reagent has three important advantages over Cr (VI) compounds. First, there are no hazardous waste disposal problems; the end products are the desired ketone and chloride ion, whereas Cr (VI) oxidations yield Cr (III) compounds known to be toxic to freshwater aquatic life. Second, Cr (VI) compounds are skin and membrane irritants, the use of bleach offers no comparable health hazards other than a small amount of Cl₂ gas, which can be contained relatively easily. And third, the cost of reagents is considerably lower for hypochlorite solutions than for Cr (VI) compounds.

Mechanism

The reaction

\[
\text{OH} \quad \text{NaOCl} \quad \text{O} \quad + \text{NaCl}
\]

is slow in neutral or alkaline solutions; therefore acetic acid is added as a catalyst. The mechanism of this reaction is still something of a mystery. The requirement for acid suggests that hypochlorous acid, HOCl, might be the actual oxidizing species (although there could be other explanations for the acid requirement). In any case, kinetic and other studies suggest that the alcohol is somehow first converted to the alkyl hypochlorite:
The latter is hypothesized to undergo E₂ elimination with H₂O as the base:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H} \quad \text{O-Cl} \\
\text{ } & \rightarrow \\
\text{ } & + \text{H}_3\text{O}^+ + \text{Cl}^- \\
\end{align*}
\]

It is clear that much more research is needed before we can understand the mechanism of this reaction.

**Methodology**

Bleach (approximately 5% NaOCl, 0.74 M) is added slowly to a solution of the alcohol in glacial acetic acid (nearly pure, >99% CH₃COOH). The reaction is exothermic, and its temperature must be carefully controlled. If too high, the product ketone could react further to give

\[
\text{and/or}
\]

If too low, the yield will be poor. You will control the temperature by regulating the rate of addition of bleach to cyclohexanol.

When the reaction is complete, you will test for any excess hypochlorite with starch-iodide test paper (paper impregnated with KI and starch). In the presence of hypochlorite the following reactions occur on the test paper:

\[
\text{OCl}^- + 2 \text{I}^- + 2\text{H}^+ \rightarrow \text{I}_2 + \text{Cl}^- + \text{H}_2\text{O}
\]

\[
\text{I}_2 + \text{starch} \rightarrow \text{blue complex}
\]

This blue color indicates the presence of excess hypochlorite. Any such excess is then destroyed by adding sodium bisulfite:

\[
\text{OCl}^- + \text{HSO}_3^- \rightarrow \text{Cl}^- + \text{HSO}_4^-
\]

\[
\text{bisulfite} \quad \text{bisulfate}
\]
The product can be separated from the reaction mixture by steam distillation, but before this is done the acetic acid must be converted to its anion so that it will not also steam distill:

\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

Finally, the product is separated from the water with which it codistills and then dried.

Note that most of the unreacted cyclohexanol is not removed (its BP is only slightly above that of cyclohexanone) and will therefore contaminate the product. By carrying out a GC analysis you will determine the percentage of unreacted alcohol remaining in your product.

The 2,4-dinitrophenylhydrazone derivative of cyclohexanone can (It will not today) be prepared and recrystallized and its melting point taken. The mechanism of its formation is worth considering. The first step is a typical addition to a C=O bond. The resulting intermediate, with OH and NH groups on the same carbon, is unstable and loses H\(_2\)O to form the C=N compound.

In preparation for this experiment, study sections 10.4-10.7 of Loudon and answer (as an exercise) the pre-lab questions on the form that follows the text of this lab. You should also find and print out the apparatus for this reaction. It can be found on the Bryn Mawr College Organic Chemistry Web Site. This lab is a practical, so the only work that will be turned in are your results, i.e., your name, product, mass of product, GC results, IR spectrum and chromic acid results.

**Procedure**

1. Assemble and apparatus consisting of a 100 mL round-bottom flask and a Claisen adapter fitted with an addition funnel (with stopper) and a condenser. Gently place a magnetic stirring bar in the flask and set up a magnetic stirrer under it. On top of the condenser place a curved adapter connected by rubber tubing to a gas trap, which in turn is connected to the vacuum line. Turn on the vacuum and water.

2. Take the flask to the hood and place in it 0.038 mole of cyclohexanol (you calculate the volume from the molecular weight and density) and 2.0
mL of glacial acetic acid. Reattach the flask to the apparatus. Detach the addition funnel (temporarily stoppering the side arm of the Claisen adapter) and place 57.5 mL of chlorine bleach in the funnel. Replace the stoppered funnel on the apparatus.

3. Turn on the stirrer and run in an estimated 5-8 mL of bleach from the funnel. A reaction should take place with the evolution of heat. Continue to add the bleach at the rate of about a drop a second, over the course of about 10 minutes. After the addition is complete continue stirring for 25 minutes.

4. To test for excess hypochlorite ion, put a drop of the reaction mixture onto starch-iodide test paper. If a dark blue color appears, add about 1 mL of saturated NaHSO₃ solution to the flask, stir, and test again. Repeat until all the hypochlorite is destroyed. (If you want to see what a positive test for hypochlorite looks like, put a drop of diluted bleach on the indicator paper. Undiluted bleach will decolorize the indicator.)

5. Add about 5 drops of thymol blue indicator solution to the flask. With the stirrer on, add 6 mL NaOH until the yellow color changes permanently to deep blue (about 5-10 mL will be required).

6. Carry out a simple distillation of the mixture, collecting the distillate in a graduated cylinder. Stop collecting when the drops of distillate are running clear, at which point the temperature at the head will have risen to about 100 °C (It is important not to collect too much water because the product is somewhat water soluble.)

7. Saturate the aqueous phase by adding about 0.2 g of solid NaCl per mL, of aqueous (lower) phase. Stir to dissolve the salt, transfer to a separatory funnel, and discard the aqueous layer. Dry the product over anhydrous MgSO₄ and filter it through a small plug of glass wool in a stemless funnel into a tared vial.

8. Test your product for purity by the chromic acid test (procedure given below). What result do you expect if your product is contaminated with cyclohexanol? If it is uncontaminated?
**Chromic Acid Test:**
In a test tube, dissolve 1 drop of your cyclohexanone in 1 mL of reagent grade acetone, then add one drop of the chromic acid reagent and mix. Primary alcohols, secondary alcohols and aldehydes form an opaque green-blue suspension within ten seconds. Ketones such as cyclohexanone should not react in such a short time period. Realize that most compounds will **eventually** react with a such a strong oxidizing agent.

9. Obtain an IR spectrum of your product.

10. Analyze your product by GC to determine how much, if any, unreacted cyclohexanol remains.

If to comprehend is the same as forming an image, we will never form an image of a happening whose scale is a millionth of a millimeter, whose rhythm is a millionth of a second, and whose protagonists are in their essence invisible.

   -- Primo Levi, *The Periodic Table*

++++++++++++++++++++++
A. Regarding the 9a procedure, how does titration with NaOH keep the acetic acid from distilling over?

B. Write a reasonable ionic mechanism (arrow formalism) describing the formation of the 2,4-DNP derivative of cyclohexanone given the following equation.

Try to work this mechanism out on your own. It is a more beneficial mental exercise than looking it up. If you get stuck, you can consult Loudon.
Name: ________________________________ Date: ________________________________

TA: ________________________________ Lab 9

Report Form

A. GC Trace (staple to report) (15 points)

B. IR Trace (staple to report) (15 points)

C. Mass of Product (10 points)

D. Chromic Acid Results (5 points)
Post-lab Questions (good practice problems may be assigned in lecture):

A. Balance the following redox reaction. (8 points)
B. Redox reactions are very important in metabolic pathways. Consider the conversion of malate to oxaloacetate (a step in the citric acid cycle). (4 points)

\[
\begin{align*}
\text{malate} & \quad \xrightarrow{NAD+} \quad \text{oxaloacetate} \\
\text{NAD}^+ & \quad \text{NADH} + \text{H}^+ \\
\end{align*}
\]

In this reaction, which species is being oxidized and which is being reduced?

C. In your own words, describe how HOCl (hypochlorous acid) acts as an oxidizing agent, i.e., by what process the electrons are removed from the alcohol. What is the oxidation state of Cl in hypochlorous acid?
D. Predict the products to the following reactions. Include **stereochemistry** where appropriate. If a reaction does not appear possible under the given conditions, simply write no reaction. (4 points - 2 points each)

(Write all possible stereoisomers)

1. 

2. 

4. 

\[ \text{H}_2\text{CrO}_4 \quad \Delta \]

\[ \text{K}_2\text{Cr}_2\text{O}_7 \quad \text{H}_2\text{SO}_4 \]
Specific Point Breakdown
Experiment 9: Oxidation of Cyclohexanol to Cyclohexanone
Not applicable to lab this year

NOTE: This report is worth 166 points

Notes for Grading Lab Reports Pre-lab

Exercises - 20 points total
A. 8 points
B. 12 points

II. Pre-lab write-up - 48 points total

Point breakdown:

10 points for introduction
4 points for main reactions (oxidation)
12 points for writing mechanism for oxidation. The students should use the arrow formalism and show all intermediates.
8 points for the side reactions for oxidation
8 points for purification of cyclohexanone
8 points for the completed table of reagents for oxidation
6 points for the completed table of products for oxidation

III. Completed Lab Report - 58 points total

6 points for observations and data
points for results

Breakdown:

2 points for 2,4-DNP derivative m.p. range
2 points for yield in grams of cyclohexanone 2 points for yield in moles of cyclohexanone
4 points for percent yield calculation for cyclohexanone 2 points for product appearance of cyclohexanone
4 points for IR spectrum and assignment of major peaks in functional group region for cyclohexanone
2 points for chromic acid test results for cyclohexanone
2 points GC retention times and identification of GC peaks for cyclohexanone 2 points for reporting composition of product mixture for cyclohexanone
30 points for conclusion

Breakdown:

10 points for explanation of deviation of yield from 100%
10 points for summary of evidence supporting identity of product
10 points for discussion of purity of product and possible sources of contamination

IV. Answers to Assigned Problems - 20 points total

A. 8 points
B. 4 points
C. 4 points
D. 4 points (2 points each)

V. Products- (Quality) - 20 points total

5 points for yield of product
5 points for purity of product
4 points for appearance of product

6 points for yield, appearance and m.p. of derivative