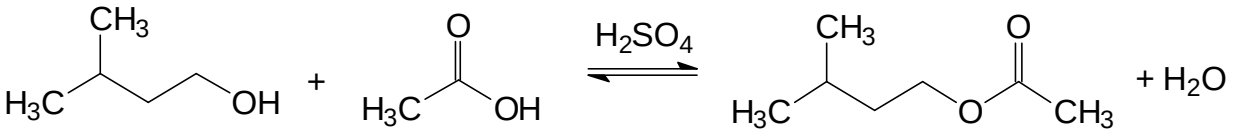
AN ESTERIFICATION REACTION.
PREPARATION OF ISOAMYL ACETATE

THE PROBLEM TO BE INVESTIGATED: Isoam**yl** acet**ate** (3-methylbut**yl** ethan**oate**) will be synthesized from isoam**yl alcohol** and acet**ic acid** by removing water as an **azeotrope**.



Eq 1

BACKGROUND INFORMATION: Some of the world's highest paid chemists work with fragrances. The mystique of the perfumery profession involves the proprietary blends of esters and all that stuff which find some use in our society. Commercially, esters are produced by **Fisher esterification**. This reaction is an acid-catalyzed process involving the corresponding **alcohol** and **carboxylic acid**. The process is an application of Le Chatelier's principle, which teaches us that if one component (H_2O) of a dynamic equilibrium is (for example, in this case) removed, the reaction will tend to shift in that direction. In Organic Chemistry II, we shall see later an alternative method for the preparation of esters utilizing an alcohol and an **acyl halide** (acid halide). This reaction is similar to that employed in the preparation of acetanilide.

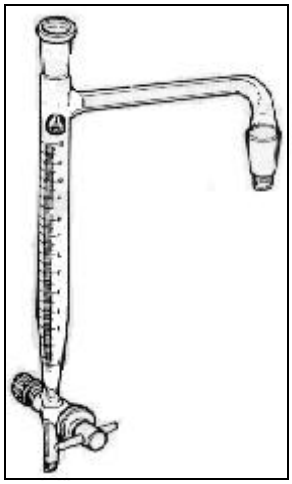


Figure 1

THE NATURE OF THIS INVESTIGATION: Since an **ester** is derived from the corresponding **alcohol** and **carboxylic acid**, **hydrolysis** of the product of formation also occurs with the same catalyst. This reversion may be circumvented by removal of either of the products. In practice, water is normally co-distilled as an **azeotrope** using a solvent such as benzene or toluene. We shall observe Le Chatelier's principle in action as the water which is produced from the reaction "settles out" and fills the sidearm adapter as the reaction progresses at **reflux**. In synthetic operations, a device known as the Dean-Stark adapter (Fig. 1) is an attachment which collects and measures the volume of water liberated from the reaction. A crude (but, inexpensive and efficient) modification will be utilized in this experiment. While distilling the product in this experiment, note and describe any aroma which may permeate your environment.

PRELAB EXERCISE: The practice of tabulating the reagents with respect to volume, weight, specific gravity, moles used, boiling points, *etc*. should help in preparing you for the experiment. The calculation of theoretical yields (on **Data Entry** page) of products should be done prior to the experiment. The actual amount of water produced in this reaction can be correlated with your calculated amount.

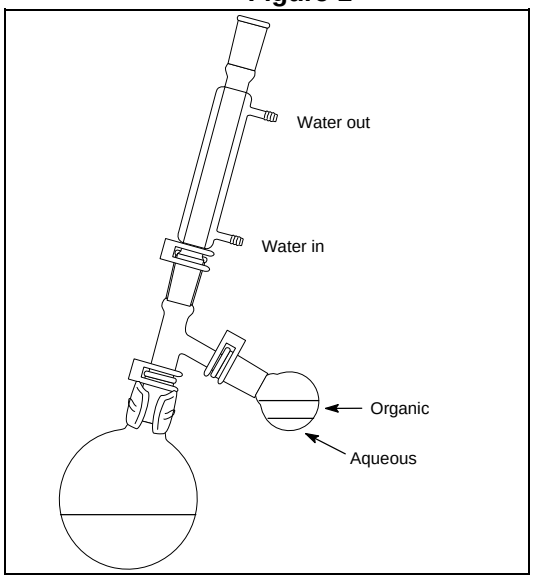


Figure 2

PROCEDURE

Into a 50 mL flask, add 12 mL glacial **acetic acid** (d. 1.05), 15 mL **isoamyl alcohol** (d. 0.81), 2 drops of concd **H_2SO_4**, and a boiling chip. The adapter head -- plugged with a modified trap (rubber adapter and sealed pipet) to the side arm -- and reflux condenser are fitted as shown in Fig. 2. The reaction flask is clamped (extension) to the ring stand such that the angle (*ca.* 50-70°) of the condenser is appropriate for the refluxing condensate to flow into the sidearm-attached trap.

About 30 minutes are required from the initial boiling. As the modified trap begins to fill, the top organic layer may be "rocked back" into the reaction flask from time to time. The bottom water layer is retained in the sealed trap (see **Helpful Hint**).

The heater is removed, the reaction flask cooled (ice water may be used), and the contents poured into the 125 mL addition (or separatory) funnel. Remove the side-arm trap and, using a 5-10 mL graduate cylinder, measure the water produced in the reaction. Record the volume of water produced in the reaction and record the approximate pH using pH paper. The remaining contents (top layer) may be added to the separatory funnel.

Add *ca.* 10 mL tap water and wash the ester to remove most of the acids. Separate and discard the aqueous wash. Repeat water wash. To the remaining ester in the funnel, add *ca.* 20 mL 5% $NaHCO_3$ solution, swirl the contents (caution!!), stopper the funnel and continue the agitation with release of any pressure generated by CO_2 gas. Separate and discard the bottom layer again. The ester is then washed with *ca.* 15 mL brine (satd. aqueous NaCl) solution, the bottom layer discarded, and the ester dried over anhydrous $MgSO_4$ for about 10-20 minutes. Decant the ester into a 25 mL RBF, add a boiling chip, and distill at atmosphere pressure. The fraction boiling over 132 degree should be collected (record the actual boiling range collected) in a tared flask. [**Note**: Do not distill to dryness -- as it is a common practice to avoid explosions. Peroxides are often unstable and, if present, will be detonated if given a chance.]

Weigh the tared flask containing your product. The IR spectrum should be recorded before turning in the product. Report the percentage yield and comment on the similarities between the IR spectra of your **cyclohexanone** and **isoamyl acetate** samples. Comment also on the weight of water produced in the reaction.

Helpful Hints - ISOAMYL ACETATE

* In the aqueous washes, water alone does not quantitatively remove the inorganic and organic acids.

* The pH of the sodium bicarbonate wash should be checked. If the aqueous solution is still acidic, more bicarbonate solution should be used in another wash until all acids are removed.

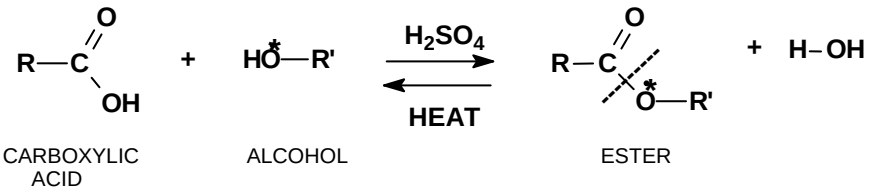
* The Dean-Stark adapter has a stopcock to release (remove) the lower water level from the top organic layer. In your case, the top organic layer is "rocked back" into the reaction flask. The principle is the same although our modification is rather crude.

* The same condenser used in reflux may be used in distillation. However, the internal walls of the condenser tube must be dried by inserting a couple of paper towels (rolled together) into it.

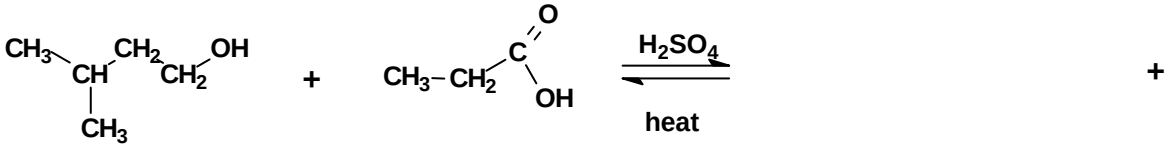
* In comparing your IR spectra as requested above, note the differences between the two carbonyl functional groups. We will examine the infrared region later when spectroscopy is discussed in lecture.

PREPARATION OF ISOAMYL ACETATE - HOMEWORK QUESTIONS

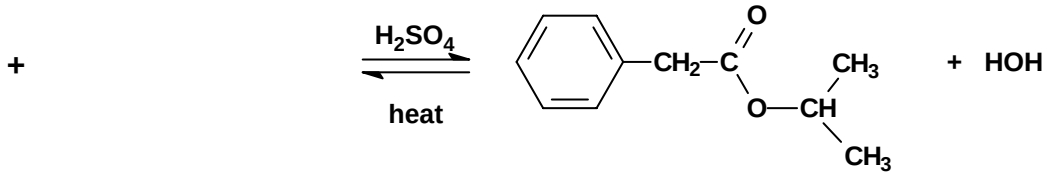
The general equation for the Fischer esterification reaction involving any carboxylic acid and any alcohol is given below. Complete the equations with the required structures. You should be able to determine that **R** comes from the carboxylic acid and the **R'** is part of the alcohol portion of the ester.



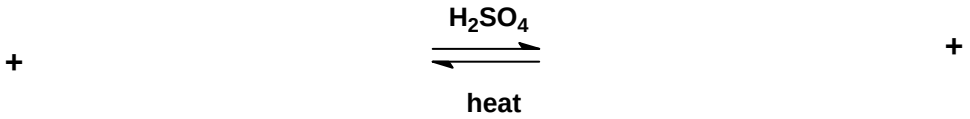
1. Complete and balance the following equation



2. Complete and balance the following equation



3. Give the **names and structures** for the two reactants required to prepare **methyl benzoate.** Also give the structure of the ester. (Hint: the ester is used as the starting material in the nitration of methyl benzoate).



Methyl Benzoate

4. Describe **two** conditions or procedures that can be used to shift the equilibrium to the right in the Fischer esterification reaction.