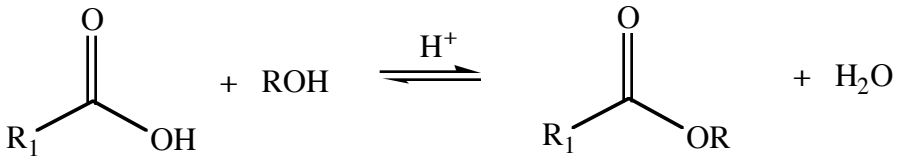
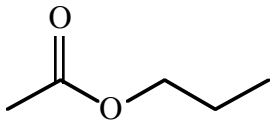
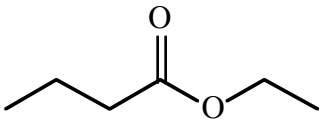
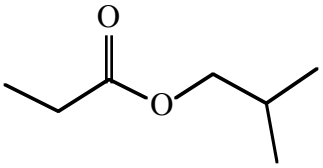
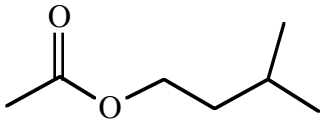
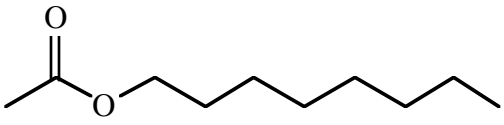
Fischer Esterification

Reaction:



Ester, Boiling point (°C), odor	structure
propyl acetate, 101.7, pear	
ethyl butyrate, 121, pineapple	
Isobutyl propionate, 136.8, rum	
Isoamyl acetate, 142, banana	
octyl acetate, 210, orange	

Introduction:

Esters are an important class of compounds widely distributed in nature. Long chain esters are the primary components of most fats and oils. The simple esters tend to have pleasant odors, and in many cases the characteristic flavors and fragrances of flowers and fruits are due to esters. Often the flavor or aroma is due to a complex mixture of esters in which a single ester predominates. Many food and drink manufacturers use these esters to add flavor to their product (as in "contains the natural flavor..."). You might think that esters are used in perfumes or scents that are applied to the body. This is only the case for the cheapest perfumes or "toilet water" (an occasionally used European term that conjures up an unfortunate image). This is because on contact with the sweat (water) on your body, the reverse reaction of the Fischer Esterification

(called hydrolysis) occurs. This produces the corresponding carboxylic acids, which are generally foul smelling compounds. Butanoic acid has a strong odor like that of rancid butter, and it is a component of what we refer to politely as "body odor". Bloodhounds are trained to follow small traces of this odor, which helps them to find us "foul-smelling" humans.

The Fischer Esterification is a readily reversible reaction, and the Keq for the forward reaction shown on the previous page is approximately 3-4. Which means that we would have a majority of the products present at equilibrium, but we would still have significant amount of the starting materials present as well. So to obtain a good yield, we will remove water using an azeotropic distillation. This will drive our equilibrium towards our products, and will enable us to obtain a good yield of the sweet smelling ester! You will get to decide which ester you would like to synthesize, and can choose your alcohol and carboxylic acid accordingly. When looking up the different starting carboxylic acids, keep in mind that many of the smaller carboxylic acids are listed by their common names. Ethanoic acid is called acetic acid. Propanoic acid is called propionic acid. And butanoic acid is sometimes called butyric acid.

Experimental Procedure

In a 5-mL short-necked round-bottom flask, place 10 mmoles of your alcohol, 10 mmoles of your carboxylic acid, 2 drops of concentrated sulfuric acid, and a couple of boiling chips. Assemble your apparatus as shown in this handout. Heat the mixture at reflux, using a sand bath heated to about 150 - 200 °C (depending on the ester you choose). The distillate will collect in the side arm as is shown in the figure. The water forms an azeotrope with the organic compounds, and the distillate in the side arm will form two layers. The lower layer will be the water. The reaction is complete when the lower aqueous layer is no longer increasing in size and both layers remain clear. This should take about 30 min. After the reaction is complete, allow the reaction mixture to cool to room temperature, and carefully tip the apparatus to allow most of the upper layer in the sidearm to run back into the reaction flask.

Transfer the reaction mixture to a tared centrifuge tube and determine the mass of your product at this point. Then slowly add 0.5 mL of saturated sodium bicarbonate to the centrifuge tube. Stir the mixture gently until the bubbling is no longer vigorous. Cap the centrifuge tube, and shake it gently (occasionally open the tube to release any pressure) until carbon dioxide is no longer being produced. Remove the lower aqueous layer, and repeat this with another 0.5 mL of saturated sodium bicarbonate solution. Remove the aqueous layer, transfer the remaining organic layer to a dry container (you should determine the mass of your product at this point), and then dry the ester with a small amount of magnesium sulfate (or granular sodium sulfate if we have it). Remove your product from the drying agent (you may need to filter your product using a tiny plug of cotton wool in a disposable pipet), analyze your product by GC, and obtain an IR and an NMR of your product. When determining your percent yield, keep in mind the ratios of materials in your reaction mixture as determined by your GC analysis.