

# Synthetic Organic Chemistry: Preparation of an Alkene by the Dehydration of an Alcohol.

# Objectives

- To learn how to assemble and use a fractional distillation glassware set-up.
- To learn how to use a separating flask to wash an organic hourd with an aqueous one and then to separate them.
- To learn how to dry an organic liquid with magnesium sufface.
- To understand the reaction being performed
- To understand which alkene will be the major product arising from the dehydration of an alcohol.
- To be able to calculate the yield of a reaction
- To interpret the infrared spectrum of the starting alcohol and of the alkene product.

# Introduction

Alkenes are organic molecules which, in their simplest forms, contain only carbon and hydrogen.

Alkenes contain fewer hydrogen atoms that the corresponding alkane (general formula  $C_nH_{2n+2}$ ) and are therefore termed unsaturated hydrocarbons.

The defining characteristic of an alkene is the presence of a functional group which is a carbon-carbon double bond.

Many naturally occurring chemicals are alkenes.

For example, ethene is a plant hormone which promotes ripening and flowering (it is used to promote the ripening of tomatoes and is given off by ripening fruit, which is why it is inadvisable to store fruit with flowers because the latter will wilt prematurely).

Another alkene,  $\alpha$ -pinene is found in pine needles and is a major component of turpentine.

NB. if no rings are in the molecule the general formula of an alkene is  $C_nH_{2n}$ .



Also, the orange carotenoid plant pigments, such as  $\beta$ -carotene (which is metabolised to form vitamin A), belong to the class of organic chemicals called alkenes.

Alkenes are important industrial chemicals.

Some of the very many important chemicals that ethene is used to manufacture are: ethanol (*i.e.* alcohol that can be consumed), acetic acid (vinegar), ethylene glycol (a component of some antifreeze agents), vinyl chloride (the starting material for PVC production) and polyethylene, to name but a few.

Alkenes are also important for the synthetic chemist. They can undergo many useful reactions which may generate compounds which could well be intermediates *en route* toward a chemical which cannot be made directly.



There are two main ways by which alkenes may be synthesised; (i) the dehydrohalogenation of alkyl halides and (ii) the dehydration of alcohols; both are elimination reactions.

Throughout the chemical industry the use of 'trivial' names for compounds is common. The more informative systematic names are preferred by chemists. Unfortunately, it is necessary to know both for some of the more frequently used compounds.



The second of these synthetic routes will be used in this experiment.

2-Methylcyclohexanol will be dehydrated with phosphoric acid  $(H_3PO_4)$  to give an alkene product.



## **Experimental Design**

Students will work individually.

After mixing the reagents together, the flactional distillation apparatus should be assembled (see below) and, using this, the reaction mixture will be heated.

The reaction products will distil ever into the receiving flask.

From these products, the organic product (an alkene) will be isolated, washed with water and then with aqueous sodium hydroxide (to remove any remaining traces of acid) and then dried with magnesium sulfate powder.

The mass of product obtained should be ascertained.

# Experimental Procedure.

### The Reaction.

Carefully pour out - with the use of a funnel - **0.20 mole** of 2-methylcyclohexanol (density 0.94 g cm<sup>-3</sup>) into a measuring cylinder NB. you will have to calculate how much 2-methylcyclohexanol you need.

Pour this into a 100 cm<sup>3</sup> quickfit roundbottomed flask (again using the funnel).

Carefully and slowly add 5 cm<sup>3</sup> (use a measuring cylinder and funnel) of the 85% phosphoric acid and gently swirl the mixture until it is homogeneous.

Add **2** boiling chips (anti-bumping granules) to the flask and then clamp it into place in an oil bath which is placed upon a stirrer hot plate, which itself is supported by a lab jack. Do not allow any oil to be displaced from the bath





Phosphoric acid is toxic and
extremely corrosive. Wear
rubber gloves at all times when
handling this acid.



(remember Archimedes). Add a magnetic stirrer bar to the oil bath.

Assemble the glassware for a distillation using a thermally lagged fractionating column (see below).



Switch on the sturrer hotplate so that the oil is stirred slowly and adjust the heating rate so that the distillation also proceeds slowly.

The distillation takes a bit of time. Keep a eye on it but make preparations for the next part of the experiment. Aim for a rate of distillation which allows the collection of products at 1 to 2 drops per second.

Maintain the distillation until all material boiling below 116 °C has been collected: but **do not** let the distillation flask boil dry. Record the boiling range that you

obtain.

Stop the distillation when a volume of material about  $10 \text{ cm}^3$  or less remains in the distillation pot.



#### Isolation / Purification of the Product.



Test that the stop-cock of a  $100 \text{ cm}^3$  separating flask functions correctly (*i.e.* is the correct size and revolves smoothly). Clamp it to a retort stand (use a special *ring* clamp) and place a beaker below it (this is a safety precaution, to catch any inadvertent spillages).

In the following steps, use a glass funnel to help you to transfer liquids efficiently.  $\land$ 

Transfer all of the distillate to the separating flask, allow the liquids to separate and then run-off most of the lower layer into a beaker labeled 'lower layer' (do not lose any of the upper layer).



Now stopper the flask, invert it and shake gently, releasing any pressure at frequent intervals (see below).



Be sure to hold the stopper tightly in place

Allow the two layers to separate and run the lower water layer into the beaker labeled 'lower layer'.



Now check this organic layer for any droplets of water. If any are visible, carefully use a Pasteur pipette to remove them.

Filtration through a funnel equipped with a **small** cotton wool plug can also help to remove small globules of water from an organic liquid sample. Ask a demonstrator to check your sample before moving on to the next stage.

Now dry the organic layer by adding a small amount of anhydrous magnesium sulfate (MgSO<sub>4</sub>, 1 to 2 g -about 1 teaspoon), swirl after the addition.

Magnesium sulfate will only remove the last traces of water but it acts

Avoid inhaling the magnesium

sulfate dust.

rapidly. After about 5 minutes test to judge whether the sample is dry.

Sprinkle a small portion of fresh anhydrous magnesium sulfate on to the top of the organic layer. If it falls rapidly to the bottom, the organic liquid still contains water and more desiccant has to be added.

After a further five minutes retest the layer and add even more drying agent, if required. However, if the additional magnesium sulfate gently settles to the bottom (looks a little like a gentle snow fall), the liquid is dry and the isolation procedure may be continued.

Use a funnel fitted with a fluted filter paper to gravity filter the dry organic liquid directly into a **preweighed** sample tube. Make sure all the product is collected.

Record the accurately determined mass of the product.

Submit the labeled sample tube containing all your product for assessment.

Ensure that the label is a self adhesive paper one and that it bears both your full names, the name or structure of the product, the approximate mass of the product and the date.

#### The Bromine Water Test

Use a Pasteur pipette to place a few drops of bromine water into a sample tube. Use just enough so that the colour of the solution is clearly visible.

Using a fresh Pasteur pipete, and two of three drops of your alkene product and shake the layers together. Record your observations.

Experimental Write-up.

Bromine water is very corrosive. Only use it in the fume cupboard. Wear rubber gloves.



In your write-up clearly state the mass of your product.

Write any pertinent observations that you made during the experiment (*e.g.* colour changes, boiling ranges, vigour of reaction *etc*).

Detailed analysis of the product from this reaction showed the existence of *two* alkenes, one of which was just a minor component.

Draw the full and the skeletal formulae of what you consider to be the major and the minor products of this reaction (N.B. both are alkenes).

In your own words, briefly explain why the two alkenes are produced in their respective amounts.

Ignoring the exact role of the phosphoric acid and considering only the major components, write the equation of the reaction (use skeletal Consult a demonstrator if you are unsure about the use of magnesium sulfate and judging the dryness of your organic layer.

Conclus



formulae).

Calculate the percentage yield of your reaction (lay the calculation out in annotated, logical steps; see below).

Draw the full and the skeletal formulae of what you consider to be the products arising from the bromine water test.

Clearly state the positions (in cm<sup>-1</sup> units) of the important signals seen in the Infrared spectrum of the starting material (see below).

Indicate which functional groups are responsible for these.

Repeat the exercise for the Infrared spectrum of the product.



#### Yield of a Reaction.

i) Write the balanced equation for the reaction.

ii) Calculate the amount (in moles) of each of the reactants and of the product that has been formed.

iii) Looking at the reactants, ascertain which is the limiting reagent *i.e.* which of the reagents is *not* in excess (which reactant is present in the smallest amount, the smallest number of moles).

The number of moles of the limiting reagent must correspond to the maximum number of moles of product that can be formed in the reaction.

iv) Divide the number of moles of product formed by the number of moles of the limiting reagent, multiply by 100.

### The Infrared Spectrum of 2-Methylcyclohexanol

The abscissa (x-axis) is calibrated in  $cm^{-1}$  units and the ordinate (y-axis) in units of % transmittance.



Peak position / cm <sup>-1</sup>	% Transmittanc
3371	25
2932	20
2854	24
1450	27
1371	33



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July 2002, we expect ca. 9 students Materials list: 2-Methylcyclohexanol (ca. 25 cm<sup>3</sup> per student) Conc. Phosphoric acid (85%) (ca. 5 cm<sup>3</sup> per student) Aqueous sodium hydroxide (5% w/v) (ca. 10 cm<sup>3</sup> per student) Dried magnesium sulfate Bromine water (freshly made so that is obviously coloured) Wash bottle containing deionised water Wash bottle containing deionised acetone Antibumping granules Silicone grease Cotton wool Filter paper (size commensurate with medium funnel) Self adhesive labels Disposable rubber gloves (all sizes) White tissues (for wiping up small spillages) Non-halogenated waste bottles 1 x Halogenated waste bottle **Apparatus list**: 1 x chataway spatula 2 x small glass funnels 2 x medium glass funnels 1 x 25 cm<sup>3</sup> measuring cylinder 1 x 10 cm<sup>3</sup> measuring cylinder 1 x 100 cm<sup>3</sup> B24 QF round bottom Rask 1 x medium oil bath (containing fresh silicone oil; temperature > 200 °C likely) 1 x stirrer hot plate 1 x medium Teflon coated magnetic styrer bar 1 x lab jack 2 x retort stands 4 x bosses 3 x clamps (with cork linings to jaws) 1 x lagged B24 QF Vigreux distillation column 1 x B24 QF still head (with B19 side arm and B19 thermometer port) 1 x B19 QF thermometer  $(0 - 300 \degree C \text{ range})$ 1 x B19 QF Leibig condenser 2 x long pieces of thin walled rubber tubing 1 x B19 QF 'pig' (three exit port receiver adaptor) 4 x 25 cm<sup>3</sup> B14 QF round bottom flasks 4 x B14 Keck clips 3 x small cork rings 4 x medium rubber bands 5 x Pasteur pipettes 2 x Pasteur pipette teats 1 x 100 cm<sup>3</sup> separating flask with correct size Teflon stopper  $3 \times 100 \text{ cm}^3$  beakers (with lip) 1 x ice bowl  $2 \times 50 \text{ cm}^3$  conical flask 3 x large sample tubes (with lids)