EXP2 – Synthesis of Cyclohexene by the Dehydration of Cyclohexanol

Aim:

The purpose of this experiment is to practise the synthesis of cyclohexene by dehydration of cyclohexanol and to understand the process of dehydration as an elimination reaction.

Principle:

The synthesis require an effective dehydrating agent to remove the OH group from the cyclohexanol and forms cyclohexyl cation as an intermediate; a hydrogen atom is further removed from the cation, forming cyclohexene as final product.

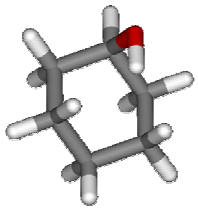
Method:

The experiment made use of a mixture of conc. sulphuric and phosphoric acid as dehydrating agent, which is characterized by the poor nucleophilic property of its anion. The reaction occurs slowly in normal conditions, but we chose to quicken it by heating. The reaction is set up under a simple distillation apparatus in order to remove the cyclohexene in the product mixture while it is formed. This prevented backwards reactions and other side reactions.

The distillates are washed with NaCl solution to remove cyclohexanol present in the product. The aqueous layer of the mixture is extracted by a separating funnel. The organic layer is further dried and purified by anhydrous calcium chloride, which could form molecule complex with cyclohexanol and water. The mixture requires further distillation to extract the dried cyclohexene.

Apparatus and chemicals:

- Cyclohexanol
- Concentrated sulphuric and phosphoric acid mixture.
- Anhydrous calcium chloride
- Saturated NaCl solution
- Ice-bath
- Boiling tubes
- Quick fit apparatus for simple distillation.
- Thermometer



Experiment Procedure and Observations

1. Some anti-bumping granules were added to a reflux flask.
2. 10 grams of cyclohexanol was placed in the reflux flask and 2.5cm^3 of concentrated sulphuric and phosphoric acid mixture was added to the flask.
3. The mixture turns orange and then brown upon mixing, heat is evolved and turns the flask warm.
4. The reflux flask was heated under a simple distillation and distillate were collected from temperature 65°C to 85°C. Distillate was collected in a boiling tube which stood in an ice bath.
5. The mixture started boiling at 60°C and its colour turned black. Some of the mixture stained on the reflux showed deep green and orange colour reflections.
6. The distillation residue was discarded into cold water and drained into a large amount of water to discard.
7. The distillate collected were is a milky liquid.
8. The distillate was transferred to a separating funnel. Saturated NaCl solution was added into it.
9. The separating funnel was shook and inverted and set still to settle.
10. The bottom aqueous layer in the separating funnel was drained.
11. Steps 8-10 were repeated once.
12. The cyclohexene was transferred to a clean test tube and about 2 grams of anhydrous calcium chloride were added to it.
13. The mixture was left for 2 days for drying to be complete.
14. The mixture was filled into a simple distillation set up and distilled, distillate were collected in temperature between 79°C to 88°C.
15. The product collected was clear liquid and able to decolourize acidified potassium permanganate and bromine water.
16. Products weight was taken down.

    Note: The mixture in step 14 were too few to carry out a further distillation. Three groups ' mixed their mixture in this step to increase batch size for a more effective distillation.

Results Recorded

Stage of Reaction	Mass	Number of Mole	Remaining percentage
Starting cyclohexanol	10.00g	0.105	100%
Crude product after first distillation	5.93g	N/A	72.3% #
Cyclohexene drained out after drying	4.53g	N/A	55.2% #
Cyclohexene before second distillation (mixed with other groups)	11.76g	0.143	N/A
Cyclohexene after second distillation (mixed with other groups)	5.62g	0.068	N/A
Component of final product originated from my group	2.08g	0.02531	25.4%

#The mass of the mixture contains impurities and does not truly represent the product. The percentage is calculated from the theoretical product yield.

Calculations

The predicted number of moles of products formed = 0.1 mol X 82.15 g mol^{-1} = 8.2 g

However, product loss due to incomplete reaction, side reactions, evaporation, spillage or residue on glassware could significantly reduce the percentage of yield.

Number of mole of actual product formed

= 2.08 g / 82.15 g mol^{-1} = 0.02531 mol

The actual product formed has 0.02531 mol. Thus the percentage yield was about 25.4% of the theoretical value.

Discussions

Introduction

In chemistry, chemical synthesis is purposeful execution of chemical reactions in order to get a product, or several products. This happens by physical and chemical manipulations usually involving one or more reactions.

Various reaction types can be applied to these to synthesize the product, or an intermediate product. Many strategies exist in chemical synthesis that go beyond converting reactant A to reaction product B.

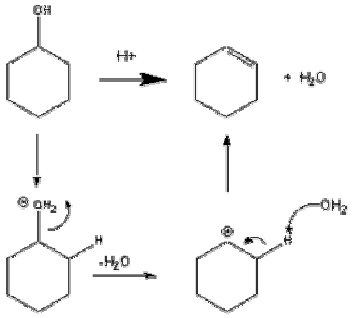
Organic synthesis is a special branch of chemical synthesis dealing with the synthesis of organic compounds. In the total synthesis of a complex product it may take multiple steps to synthesize the product of interest, and inordinate amounts of time. Skill in organic synthesis is prized among chemists and the synthesis of exceptionally valuable or difficult compounds has won chemists such as Robert Burns Woodward the Nobel Prize for Chemistry.

SYNTHESIS Journal

SYNTHESIS is a journal of international character devoted to the advancement of the science of synthetic chemistry, covering all fields of organic chemistry, such as organometallic, organoheteroatom, medicinal, biological, and photochemistry, but also related disciplines. It presents dependable research results with experimental procedures and full characterization of important new products. SYNTHESIS will be

published 24 times in 2007. Thus we see the importance of organic synthesis in the field of organic chemistry.

Characteristics of this experiment



This experiment features the dehydration of cyclohexanol and produce cyclohexene. This is the most common experiment among beginning organic chemistry students. The acid catalyzed dehydration of cyclohexanol with distillative removal of the resulting cyclohexene from the reaction mixture is a very good example to show the possibility of combining two steps in synthesis in one single step, reducing the experiment time length, and the possibilities of side reactions.

This technique of distillation of the product as it forms, is only applicable to a small group of reactions where the product of reaction have the lowest boiling point among the reactants. This technique prevents the product to contact other reactants, and leave the heating environment which might cause side reactions. The removal of the product also helps to shift the equilibrium position of the incomplete reaction to the right hand side, and prevents backwards reaction, resulting in an increased yield of products.

This experiment also introduces the idea of azeotrope. An azeotrope is a mixture of two or more pure compounds in such a ratio that its composition cannot be changed by simple distillation. This is because when an azeotrope is boiled, the resulting vapour has the same ratio of constituents as the original mixture of liquids. Each azeotrope has a characteristic boiling point. The boiling point of an azeotrope is either less than the boiling points of any of its constituents (a positive azeotrope), or greater than the boiling point of any of its constituents (a negative azeotrope).

The azeotropes of cyclohexanol/water and cyclohexene/water are both positive azeotropes. The separation of cyclohexene could not depend on distillation alone. The method used in our experiment is one way that we could employ to separate azeotropes into its constituents. By adding a chemical that could form complex with one of the component, in our case, $CaCl_2$ forms complex with water, holding water molecules together with the $CaCl_2$ solid. After distillation of the mixture, the resultant product would be dry and free of water.

Side reactions and reaction yield

A side reaction is an unwanted chemical reaction taking place that diminishes the yield of the desired product. The amount of product in a chemical synthesis is the rea ction yield. Typically, chemical yields are expressed as a weight in grams or as a percentage of the total theoretical quantity of product that could be produced.

The experiment manual suggest that possible side reaction involves the formation of polymer (tar) by the polymerization of the double-bond-possessing cyclohexene. This occurs when cyclohexene picks up a proton and forms a cyclohexane cation, which is reactive towards polymerization as follows:

Another form of side reaction might be the condensation of two cyclohexanol to form one ether. The condensation is favoured by the presence of concentrated sulphuric acid which possess a strong oxidizing power when hot. The reaction might be like this:

Due to the presence of the hot concentrated sulphuric acid, the product cyclohexene may also be subjected to further oxidation. The double bond may be oxidized to a di-aldehyde or other fragments.

In lab papers published in Organic Syntheses, Coll. Vol. 1, p.183 (1941); Vol. 5, p.33 (1925). This synthesis in our experiment, performed in lab conditions with a quantity of 400 grams of initial cyclohexanol reactant, the reaction yield should be 79% to 87% of the theoretical amount. The experiment manual suggests the yield to be about 73% when the batch size is 20 grams.

The results show that only 25.4% of final products is yield, the reason may be due to small batch size (10 grams), inefficient experiment procedures or poor lab techniques.

Notes on experiment techniques

Frequent transferring of the volatile cyclohexene product should be avoided as it is easily lost through evaporation. Careful think where the product and intermediate steps product should go in the next step, choose a reflux bottle to collect the distillate in a distillation if such distillate is expected to undergo another distillation in the next steps.

Most organic products are flammable and volatile. They should be handled in well ventilated area and prevent naked flame to reach the chemicals or its vapours. In case heating is used to increase the reaction rate, reflux setup should be employed. Always keep a stopper handy in case you wish to stop the chemical from evaporating.

When handling corrosive or highly acidic chemicals such as the concentrated sulphuric acid and phosphoric acid mixture. Rubber gloves should be wore to avoid spillage, a pipette or a dropper is recommended for the transfer of such chemicals in a specific amount. The handling of such corrosive or hazardous chemical wastes should always follow strict rules to avoid accidents or environmental pollution.

Cleaning of synthesis involved apparatus is difficult even with the use of detergent, oily organic substance are remained on the surface of glassware. From the experience gained, the apparatus may first be washed with water and detergent, followed by an organic solvent which could completely evaporate. Acetone is a good choice as it is a common solvent for most organic solvents and it is miscible with water.

THE END