

26. The preparation and purification of *N*-phenylethanamide

Student Sheet

In this experiment you will learn or develop skills in preparative organic chemistry by making and purifying a sample of an aromatic amide using an acylation reaction. You will assess the purity of your product by measuring its melting point and comparing it with the data book value. The acylating agent you will be using is ethanoic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$. This is used in preference to ethanoyl chloride, CH_3COCl , as the latter is rather too reactive for use in these circumstances.

Intended lesson outcomes

By the end of this exercise you should be able to:

- determine the weight of a material using the **weighing by difference** method
- handle hazardous materials safely
- purify by recrystallisation
- determine yield and melting point
- estimate the purity of a product

Background information

The preparation of *N*-phenylethanamide from phenylamine is termed **acylation**. Both ethanoyl chloride, CH_3COCl , and ethanoic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$ may be used as **acylating agents**. The reactivity of ethanoic anhydride is, however, lower than that of ethanoyl chloride and so allows the reaction rate to be more easily controlled.

The equation for the acylation of phenylamine by ethanoic anhydride is given below.



Phenylamine is most conveniently used in the form of the salt phenyl ammonium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$.

The reaction is performed in two stages

- 1 A solution of sodium ethanoate is treated with phenylammonium chloride forming phenylamine, ethanoic acid and sodium chloride.
- 2 Phenylamine then reacts with ethanoic anhydride to form *N*-phenylethanamide (as a white solid), together with ethanoic acid.

Aqueous solutions of phenylammonium chloride and ethanoic anhydride are mixed. To this mixture is added a second aqueous solution containing sodium ethanoate. The sodium ethanoate causes the reaction in stage 1 to occur. Once phenylamine is released, it reacts readily with ethanoic anhydride to form *N*-phenylethanamide as a white solid. The crude solid product is removed by filtration and purified by recrystallised from hot water. Typically a yield of around 70% of the theoretical maximum is obtained.

Note: An excess of ethanoic anhydride is used in order to ensure a good yield.

Questions

- Write an equation for the reaction occurring in stage 1.
- When phenylamine is treated with ethanoyl chloride, or with ethanoic anhydride, the product formed is *N*-phenylethanamide. Write equations for **both** of these reactions.

Safety

There are potentially hazardous substances involved in this exercise. You **must** follow all health and safety instructions given to you by your teacher. Materials safety data sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident.

	You must wear eye protection throughout this experiment
 	Phenylammonium chloride is toxic and dangerous for the environment . Your teacher will tell you how to dispose of it safely.
	Ethanoic anhydride is corrosive

Procedure

1. You are provided with 1.0 g of phenylammonium chloride. Dissolve this completely in 30 cm³ of water in a conical flask.
2. To this solution, add 2.0 cm³ of ethanoic anhydride.
3. Stir the mixture vigorously until all of the ethanoic anhydride has dissolved.
4. Weigh out 6.0 g of hydrated sodium ethanoate and dissolve it in 25 cm³ of water in a conical flask.
5. Add the sodium ethanoate solution to the solution from (3) and stir the mixture for three minutes. If solid fails to appear, continue stirring for a further three minutes.
6. Filter off the crude product, using the filtration apparatus provided, and wash it with a little **cold** water. **Show** this crude product to your teacher before proceeding any further.

Recrystallisation

7. Dissolve the whole of your product in the **minimum** volume of **hot** water in a boiling tube. Do this by adding hot water in small amounts until the solid dissolves. Stir the mixture with a glass rod to help the solid dissolve. When it has dissolved completely, allow the solution to cool.
8. **Note:** Your sample **may** contain some dark material that is insoluble. In this case, **do not** keep adding water. As soon as it is obvious that the bulk of the *N*-phenylethanamide has dissolved, filter the hot liquid carefully into a clean boiling tube.
9. Set your solution aside to cool.
10. When crystallisation is complete, filter off the pure product using the filtration apparatus provided. Dry the crystals between filter paper, then transfer them to a sample tube and leave them to dry in air. Label your sample tube.
11. Prepare a suitable table to record your yield and melting point.
12. Weigh your sample tube and contents. Transfer your sample into a second clean container and re-weigh the original, now empty, sample tube. This technique is known as **weighing by difference**. Enter your results in your table and calculate the mass of your product.

Test for purity

13. Determine the melting point of the substance, which should be above 100 °C. Record the melting point in your table. Show your purified sample to your teacher.

Theoretical maximum mass of product

14. Deduce, from the mass of phenylammonium chloride you used, the **maximum** mass of *N*-phenylethanamide which could be produced (i.e. if all the phenylamine had been converted into product).

Percentage yield of product

15. Deduce the percentage yield of your preparation. You do this by comparing the mass of your product with the theoretical maximum mass (from point 14) and expressing the result as a percentage.

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Teachers' Notes

The syllabus requires students to show an understanding of the chemistry of acyl chlorides. Given the hazards associated with this class of compound, the use of ethanoic anhydride provides a safer alternative to the use of ethanoyl chloride in ethanoylation reactions. Overall, the exercise provides a range of learning experiences for the student, which include: weighing and measuring, the safe handling of materials, recrystallisation techniques and melting point determination.

Intended learning outcomes

Please see the Student Sheet

A suggested approach

The exercise provides considerable opportunity for students to practice and develop their manipulative skill. It may also help them to appreciate that organic reactions, unlike many inorganic reactions, require care and patience if pure products are to be produced and that, despite all their care, yields are likely to be limited.

This exercise involves the use of potentially hazardous materials and so students should be closely supervised, unless they have considerable experience of organic preparations.

The use of vacuum filtration, using a Buchner filtration system, is preferred. The exercise may be successfully complete using gravity filtration, but it does take longer; especially in the final drying stage.

A brief discussion of the chemistry involved would set the scene. The extra stability and convenience resulting from using phenylamine in the form of its solid salt, rather than as the free liquid, should be covered. Also, the necessity of releasing phenylamine from its salt prior to use provides an opportunity to discuss strong acid / salt of weak acid reactions.

The exercise can be conducted in two parts, with a break after the completion of Step 8. This would allow time for the samples to dry properly.

If the melting point of the student's sample is to be used to check purity it is very important that:

- the sample is dry
- the students do not have prior knowledge of the melting point from other sources.

An element of competition can be introduced into the exercise by publicly sealing the melting point in an envelope. After all the students/groups have declared their melting points, the envelope is ceremoniously opened and a small prize is awarded to the winner.

The data book value for the melting point of *N*-phenylethanamide is 114–116 °C

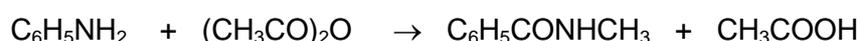
Note: It might be worth spending a little time discussing the importance of acylation reactions in general and the production of polyamides in particular.

Answers to questions

- The correct equation for the reaction occurring in stage 1 is.

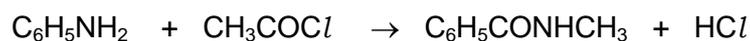


- The correct equation for the reaction between phenylamine and ethanoic anhydride is.



Appendix 2

- The correct equation for the reaction between phenylamine and ethanoyl chloride is.



- For Question 13
Maximum mass of *N*-phenylethanamide from 1.0 g of phenylammonium chloride = 1.04 g
- For Question 14
The percentage yield will be consequential on the mass obtained by the student. A yield around 70% is good. If it is higher than this then the product is likely to be impure or damp.
- Melting points should be compared with the book value of 114–116 °C. Impure samples are likely to melt over a wide range, and at a temperature lower than 114–116 °C.

Technical information

Requirements per student/group

Apparatus

- spatula
- distilled water bottle
- three 250 cm³ beakers
- small conical flask
- three boiling tubes
- 50 cm³ measuring cylinder
- 10 cm³ measuring cylinder
- glass stirring rod
- filtration apparatus, Buchner apparatus (preferred) or filter funnel
- filter papers appropriate for filtration apparatus supplied
- Bunsen burner
- tripod and gauze
- dropping pipette
- standard filter paper x 4"
- two sample tubes
- two small sticky labels
- eye protection
- access to melting point apparatus
- two melting point tubes
- access to weighing machine
- sight of Hazard card

Materials

Chemical samples should be kept in screw top bottles or sealed tubes.

- about 7 g of sodium ethanoate
- about 1 g of phenyl ammonium chloride
- about 2 cm³ of ethanoic anhydride

Safety

The main points are included on the Student Sheet. However, it is essential that a risk assessment be carried out before a decision is taken to go ahead with this exercise. MSDS sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident. Materials that are harmful to the environment must be disposed of according to local regulations.

- It must be **made clear** to students that potentially hazardous materials are in use and that precautions are needed to minimise the risk to themselves and to others.
- Your **MUST** be prepared to **intervene** if a student seems to be unsure of a procedure, or is performing an unsafe operation.