

## 19. The preparation and purification of methyl-3-nitrobenzoate

### Student Sheet

In this experiment you will learn or develop skills in preparative organic chemistry by making and purifying a sample of an aromatic nitro compound. You will assess the purity of your product by measuring its melting point and comparing it with the data book value.

#### 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 the yield and melting point of a reaction product
- Estimate the purity of a reaction product
- Write a mechanism for the electrophilic substitution reaction involved in nitration

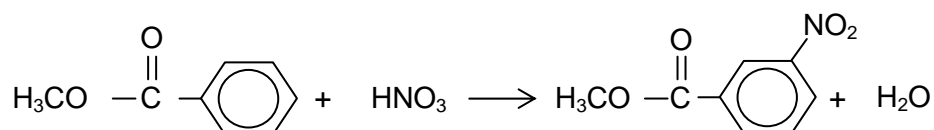
#### Background information

Nitration of an aromatic ring occurs by an electrophilic substitution reaction. The electrophile is the nitronium ion,  $\text{NO}_2^+$ , which is prepared by the reaction between concentrated nitric acid and concentrated sulphuric acid. The equation for this reaction is given below.



The reaction conditions necessary for the nitration step which follows depend on the nature of the molecule being nitrated; as does the position into which the nitro group will be substituted. Using methylbenzoate, the reaction occurs readily, so that a relatively low temperature is sufficient, and the nitro group tends to be substituted into the 3-position on the benzene ring. Great care must be taken that appropriate cooling is used, and that the hazardous materials used are safely handled. Purification of the crude product is by recrystallisation from the minimum amount of hot ethanol.

The overall equation for the nitration reaction is







Once the nitro group has been introduced into the ring, it may be readily reduced to an amine group, by heating it with tin and concentrated hydrochloric acid. This reaction sequence provides a very useful route to the synthesis of aryl amines.

#### Question

Write a mechanism for the electrophilic substitution reaction involved in this reaction, showing clearly the structure of the intermediate species formed.

#### 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
	Methylbenzoate is <b>harmful</b>
	Nitric acid and sulphuric acid are <b>corrosive</b>
	Ethanol is <b>highly flammable</b>

### Procedure

1. Measure  $9.0\text{ cm}^3$  of concentrated sulphuric acid into a dry  $100\text{ cm}^3$  conical flask and place the flask in an ice bath.
2. Add about  $4.0\text{ cm}^3$  of methylbenzoate to a small measuring cylinder. Weigh the measuring cylinder and methylbenzoate recording the mass.
3. Prepare a **nitrating mixture** by carefully mixing  $3.0\text{ cm}^3$  of concentrated nitric acid and  $3.0\text{ cm}^3$  concentrated sulphuric acid in a test tube. Place this test tube in the ice bath.
4. Add the methylbenzoate to the conical flask; swirling the flask while you do so. Weigh the emptied measuring cylinder and calculate the mass of methylbenzoate added. This process is known as **weighing by difference**.
5. Using a dropping pipette, add the nitrating mixture to the conical flask. You must swirl the flask after each addition and, by monitoring the thermometer, adjust the rate of addition to ensure that the temperature **does not exceed  $15^\circ\text{C}$** . Do not rush the addition; it should take about 10–15 minutes.
6. After the addition is finished, allow the flask to stand at room temperature for about 10 minutes. Pour the reaction mixture from the flask into a small beaker containing about 40–50 g of crushed ice. Stir until the product solidifies.
7. Filter off the impure solid product, preferably using vacuum filtration, and wash the product, first with cold water and then with about  $5\text{ cm}^3$  of ice-cold ethanol. Allow the solid to dry as much as possible.

### Recrystallisation

8. Place the impure product in a clean  $100\text{ cm}^3$  conical flask and add  $10\text{ cm}^3$  ethanol. **Gently** warm the mixture in a water bath. If some of the solid fails to dissolve add further  $2\text{ cm}^3$  portions of ethanol until it does dissolve, **but** do not continue adding ethanol if it is clear that some material is not going to dissolve; your aim is to produce as concentrated a solution as possible.
9. If necessary, filter the solution using a filter funnel or Buchner funnel to remove any insoluble material. To prevent crystals forming during filtration, pre-heat the funnel by adding hot solvent to the filter paper in the funnel; allow time for the solvent to run through. Discard this hot solvent before you use the hot funnel to filter your solution.
10. Cool the filtrate in an ice bath until crystals form.
11. Filter off the crystals, preferably by vacuum filtration, and allow them to dry as much as possible. Transfer the crystals to a clean piece of filter paper on a watch glass. Let the crystals stand overnight to dry out completely.

## Appendix 2

12. Weigh the crystals by adding them to a pre-weighed sample bottle and reweighing.
13. Using the melting point apparatus provided, determine the melting temperature of your crystals.
14. Transfer your crystals to a sample bottle labelled with your name.

**Theoretical maximum mass of product**

15. From the mass of methylbenzoate added, deduce the **maximum** mass of methyl-3-nitrobenzoate which could be produced (i.e. if **all** the methylbenzoate had been converted into product).

**Percentage yield of product**

16. Calculate the percentage yield of your preparation. You do this by comparing your actual yield of product with the theoretical maximum yield and expressing the result as a percentage.

**Purity**

17. The pure product would have a melting point of  $77\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ ; compare your melting point to this value. The further away, and the wider the melting range, your melting point is compared to  $77\text{ }^{\circ}\text{C}$  the less pure is your product. Also, your crystals should be dry and pale yellow in colour. Comment on the appearance, yield and purity of your product and then show your product to your teacher, who will also assess its appearance and yield.

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### Teachers' Notes

Overall, the exercise provides a range of learning experiences for the student, which include: weighing and measuring, the safe handling of materials, temperature control, 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 they are to be successful, and that, despite all their care, yields are likely to be limited.

It would be worth spending a little time discussing the usefulness of this reaction in the synthesis of aryl amine and their products.

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 nitration reaction proceeds readily and so, in order to prevent multiple substitution, it is necessary to cool the reaction mixture. The use of vacuum filtration, using a Buchner filtration system, is preferred. The exercise may be successfully completed using gravity filtration, however, but it does take longer; especially in the final drying stage.

### Note

The product from this reaction could be reduced to make the aryl amine. This is not advised, however, as the purity of the nitrated product cannot be guaranteed. If your students were to perform such a reduction reaction, it would be better to use a commercial sample of an appropriate aromatic nitro compound. The reaction process involves the use of concentrated hydrochloric acid, concentrated sodium hydroxide, ether extraction and steam distillation. The final purification of the phenylamine product is by distillation. This reaction sequence requires considerable practical experience but could, if wished, be performed as a demonstration. Details may be found in:

*Advanced Practical Chemistry*  
by JS Clarke & S Clynes (English University Press)

### Technical information

Requirements per student/group

### Apparatus

- Two 100 cm<sup>3</sup> conical flasks
- Large beaker/small trough/small washing up bowl for ice bath
- 100 cm<sup>3</sup> beaker for crushed ice
- Beaker for water bath
- Two/three 10 cm<sup>3</sup> measuring cylinders
- Thermometer for monitoring temperature during nitration
- Stirrer – unless the thermometer may be used for this purpose
- Buchner funnel and flask **or** filter funnel
- Filter paper for funnel and for drying crystals

## Appendix 2

- Suction pump (if Buchner system used)
- Two dropping pipettes
- The apparatus normally used for melting point determinations
- Marker pen for labelling test tubes
- Access to balance

**Materials**

- Access to methylbenzoate
- Access to concentrated nitric acid
- Access to concentrated sulphuric acid
- A supply of ethanol
- A supply of crushed ice
- Distilled/deionised water
- A supply of hot water for the recrystallisation

**Safety**

The main points are included on the Student Sheet. However:

It is essential that a risk assessment is 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.

- 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.

A number of ways in which the exercise may be made less hazardous and more likely to succeed include:

- (i) Measuring out the concentrated acids yourself and supplying them to the students in a labelled conical flask labelled A and a labelled test tube.
- (ii) Using hot water from a kettle for the water bath during the recrystallisation stage.
- (iii) Supplying small pieces of crushed ice for the ice baths.
- (iv) Telling the students that their safe working practices are being **assessed**; whether this is true or not!