

Nitration of methyl benzoate – student sheet

In this experiment you are going to synthesise a sample of methyl 3-nitrobenzoate by the nitration of methyl benzoate.

Pre-lab questions

1. Draw out the skeletal formula for methyl benzoate.
2. In the nitration of an aromatic compound, the electrophile is the nitronium ion or nityl cation, NO_2^+ .
The nitronium ion is generated in the reaction mixture of concentrated sulfuric acid and concentrated nitric acid.
Write an equation/equations to explain the formation of NO_2^+ from this mixture.
3. Outline a mechanism for the nitration of methyl benzoate to form methyl 3-nitrobenzoate.
4. The crude product can be purified by recrystallization.
Describe the key properties a solvent needs to be suitable for use in recrystallization.

Procedure

Hand protection must be worn

Goggles must be worn

Apparatus	Chemicals
conical flasks (1 × 50 cm ³ and 1 × 100 cm ³)	methyl benzoate (MODERATE HAZARD – harmful if swallowed)
balance	concentrated sulfuric acid (CORROSIVE – causes severe skin burns and eye damage)
spatula	concentrated nitric acid (CORROSIVE AND OXIDISING – causes severe skin burns and eye damage. May intensify fire)
10 cm ³ measuring cylinders × 2	methyl 3-nitrobenzoate (no known hazards)
glass dropping pipette	ethanol (FLAMMABLE – highly flammable liquid and vapour). IDA (FLAMMABLE – highly flammable liquid and vapour; MODERATE HAZARD – harmful if swallowed, may cause damage to organs) can be used instead.
ice-water bath	distilled water
glass rod	
test tube	
thermometer (0–100 °C)	
Buchner funnel apparatus	
melting point apparatus	



Preparation of methyl 3-nitrobenzoate

1. Weigh 2.0 g of methyl benzoate into a dry 50 cm³ conical flask.
2. Add 4 cm³ of concentrated sulfuric acid slowly to the methyl benzoate with swirling to ensure thorough mixing. Cool this mixture by partially immersing the flask in an ice-water bath.
3. Carefully transfer 1.5 cm³ of concentrated nitric acid into a dry test tube. Cool the nitric acid by partially immersing it in an ice-water bath before slowly adding, with swirling, 1.5 cm³ of concentrated sulfuric acid. Ensure thorough mixing. Allow this mixture to cool.

This is the nitrating mixture.

4. Using the glass dropping pipette, very slowly add the nitrating mixture (over about 15 min, 1 drop every 10 seconds) to the contents of the conical flask. Stir the reaction mixture as the addition is made. During the addition keep the temperature of the reaction mixture below 6 °C.

NOTE: The nitrating mixture is very corrosive. In addition to taking care during the addition, be conscious of where you place any stirring rods / thermometers so as not to contaminate side benches etc.

5. Once addition is complete, allow the flask containing the reaction mixture to stand at room temperature for 15 min.
6. Carefully pour the reaction mixture onto a small amount (approx. 20 g) of crushed ice held in a beaker. Stir the crushed ice throughout. Solid methyl 3-nitrobenzoate will form.
7. Allow the ice to melt and filter under suction. Wash the crude product with a little ice-cold water.

Purification and analysis

Methyl 3-nitrobenzoate is insoluble in water but soluble in hot ethanol. Therefore the crude material can be purified by recrystallization from a water/ethanol mixture.

1. Add 10 cm³ of distilled water to the crude material held in a small conical flask and warm the mixture to just below boiling point. The methyl 3-nitrobenzoate will melt at this temperature but you will be able to see an 'oily' substance within the water.
2. Slowly add hot ethanol (heated using a hot plate) 1 cm³ at a time until the 'oily' substance just dissolves.
3. Allow the mixture to cool to room temperature before cooling it further in an ice-water bath.
4. Filter the crystals under reduced pressure and allow them to dry ideally in an oven overnight (below 50 °C!).
5. Record the melting point of your sample of methyl 3-nitrobenzoate.



Analysis

1. Determine the percentage yield for your reaction. Give two reasons to explain the value you obtain.
2. Compare the melting point of your purified methyl 3-nitrobenzoate to the literature value. Is your sample pure? What impurities might be present?

Extension

Nitration of methyl benzoate is selective for the 3-position. Carry out some research to find out why.

