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LAB REPORT ON THE PREPARATION OF METHYL-3-NITROBENZOATE AND NITROGUANIDINE

References. See footnotes and embedded documents section at end of document.

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1. Introduction and Background

This report details the preparation and results of nitration to create methyl-3-nitrobenzoate and nitroguanidine conducted by the student on 19th November 2025. This report is broken down into 2 stages the first is the preparation of Methyl-3-Nitrobenzoate and the second is the preparation of Nitroguanidine.

2. Methyl-3-Nitrobenzoate

2.1.Introduction

Methyl-3-Nitrobenzoate is an intermediate chemical compound used in the formation of several dyes, pesticides and pharmaceutical medication.

2.2.Experiment Purpose

The purpose of the preparation of Methyl-3-Nitrobenzoate (MNB) was to demonstrate the process of aromatic ring nitration, this is that same process as that used to form DNT an primary precursor to TNT. In addition, it introduced and demonstrated the procedure of nitration whilst controlling temperature and acting in a safe manner for the later preparation. This allowed for the safe practice of the later N-Nitration to form the explosive compound nitroguanidine.

If toluene was used instead of Methyl benzoate there would be three likely formations, 2 types of Nitrotoluene and dinitrotolurene (DNT) these are pictured below.

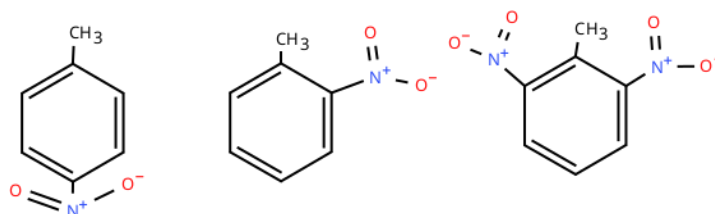


Figure 1 - MNT and DNT formations

2.3.Predictions

The experiment involved the nitration of Methyl-3-Nitrobenzoate by using the electrophilic substitution of NO_2^+ , this is detailed below.

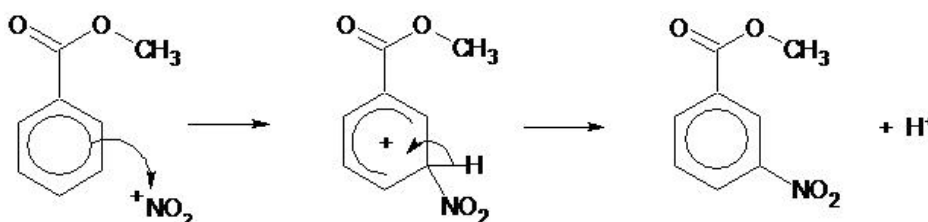


Figure 2 - Electrophilic Substitution of Methyl-3-nitrobenzoate [1]

It was predicted that a low yield would be observed due to the inexperience of the students in these procedures. Despite this the demonstrative purpose of the experiment would be realised.

2.4.Procedure

The full setup and procedure can be found at Annex 1.

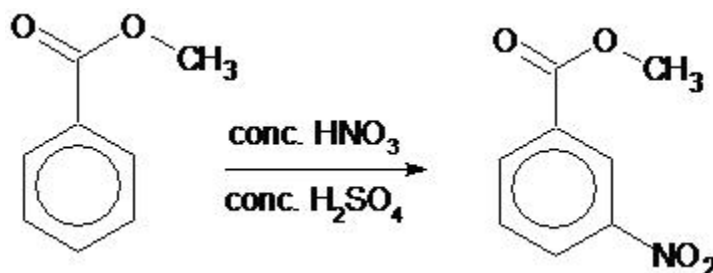


Figure 3 - Overall Reaction 1 [1]

During the nitration Sulphuric and nitric acid was used as the reagent as it acts a catalyst for the reaction. During this process of nitration it is critical to keep the mixture cool to ensure a proper rate of reaction and an even nitration of the constituent parts. It also prevents a runaway reaction that is uncontrolled and could lead to initiation in an energetic material.

The full balanced chemical equation for this reaction can be seen in Equation 1



At the recrystallization stage Ethanol was used as Methyl-3-Nitrobenzoate is not soluble in water.

2.5.Results

Quantity Name	Shorted Name	Mass (g)
Mass of methyl benzoate	MB	2.694
Mass of labelled glass bottle		8.639
Mass of labelled glass bottle + Dried sample		11.504
Mass of methyl-3-nitrobenzoate	NB	2.865
Molar Mass of methyl benzoate	Mr (MB)	136.15
Molar Mass of methyl-3-nitrobenzoate	Mr (NB)	181.15
Theoretical Yield		3.58
Actual Yield		2.865

$$\text{Equation 2 - Theoretical Yield} = \text{MB} \times \frac{M_r(\text{NB})}{M_r(\text{MB})}$$

Using Equation 2 a theoretical yield of 3.58g can be calculated for this preparation

$$\text{Equation 3 - \% yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 \quad [2]$$

Using Equation 3 a percentage Yield of 80.02% is achieved.

3. Nitroguanidine

3.1.Introduction

Nitroguanidine (NQ) is a secondary explosive primarily used in large calibre gun propellants. These propellants are referred to as triple base and the addition of NQ cools the deflagration reaction which in turn reduces stress and wear on the gun barrels. [3] [4]

The guanidine nitrate produced in this experiment is likely to be long crystals. These would need to be ground down into a powder for further use in double based propellant. This would create a uniform grain size and therefore a uniform reaction rate. [5]

3.2.Experiment Purpose

The purpose of the preparation of NQ was to demonstrate the synthesis of explosive and further expand the students understanding of the chemical procedures of N-nitration.

3.3.Predictions

The experiment involved the N-nitration of Guanidine Nitrate to form Nitroguanidine. The nitration used sulfuric acid to facilitate the reaction with the biproduct of water. It was predicted that a low yield would be observed due to the inexperience of the students in these procedures. Despite this the demonstrative purpose of the experiment would be realised.

3.4.Procedure

The full setup and procedure can be found at Annex 2.

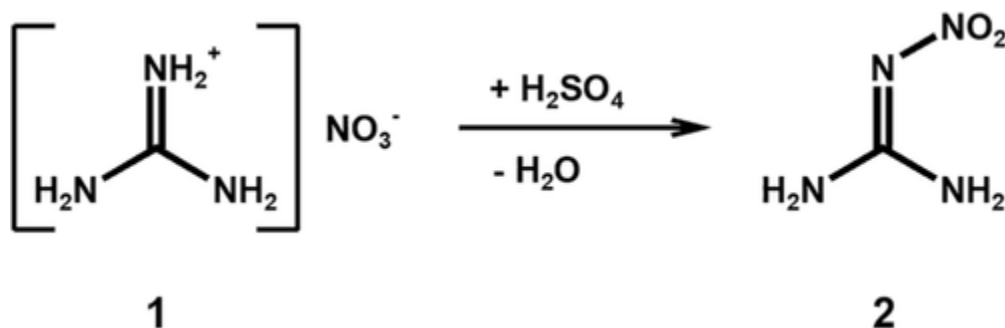
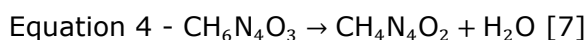


Figure 4 - Overall Reaction 2 [6]

During the nitration only Sulphuric acid was needed as the catalyst as the guanidine nitrate already has the nitrate group to use. During this process of nitration it is critical to keep the mixture cool to ensure a proper rate of reaction and balanced nitration of the constituent parts. It also prevents a runaway reaction that is uncontrolled and could lead to initiation in an energetic material.

The full balanced chemical equation for this reaction can be seen in



3.5.Results

Quantity Name	Shorted Name	Mass (g)
Mass of labelled glass bottle		92.090
Mass of labelled glass bottle + Dried sample		94.242
Mass Guanidine Nitrate	MGN	4.000
Mass of Nitroguanidine	MNQ	2.334
Molar Mass Guanidine Nitrate	MrGN	122.08
Molar Mass Nitroguanidine	MrNQ	104.07
Actual Yield		68.45

$$\text{Equation 5 - \% yield} = \frac{MNQ}{MGN} \times \frac{MrGN}{MrNQ} \times 100$$

Using Equation 5 a percentage Yield of 68.45% is achieved.

4. Conclusions

The two experiments were largely a success, demonstrating the synthesis methods and developing practical skills. The ideal colour of both substances is a brilliant white. The two samples were both slightly off coloured, this is likely due to the main contaminant being methyl benzoate and guanidine nitrate respectively.

The percentage yields for each nitration were 80.02 and 68.45% respectively. This shows a significant decrease in yield for the second experiment. This demonstrates that the inexperience of the student is not a likely cause of the decrease.

The final recrystallization stage for the NQ was tricky as the final crystals clumped and stuck to the funnel and could not be washed at this stage. Consequently, this meant that a small proportion of the final crystals were lost to contamination of the glassware.

The key methods to improve these yields would be to further control the temperature of the reaction, reducing the quantity of the recrystallization solute and ensuring a complete nitration of the base products.

5. References

- [1] C. Smith, "Nitration of methyl benzoate," [Online]. Available: <https://edu.rsc.org/resources/nitration-of-methyl-benzoate/2323.article>. [Accessed 26 11 2025].
- [2] BBC, "Factors affecting the yield of chemical reactions," BBC, [Online]. Available: <https://www.bbc.co.uk/bitesize/guides/ztbqfcw/revision/3>. [Accessed 27 11 2025].
- [3] M. WARMAN, S. SEMEL, J. LECCACORVI, R. MOTTO and R. HUTCHINSON, "CONVERSION OF GUANIDINE NITRATE TO NITROGUANIDINE WITH RECYCLE OF SPENT ACID," Technical Library, 1975.
- [4] P. Worsfold, A. Townshend and C. Poole, Encyclopedia of Analytical Science, Elsevier Ltd, 2005.
- [5] N. L. o. Medicine, "Production of nitroguanidine from guanidine nitrate by the action of aqueous sulphuric acid," 2025.
- [6] E.-C. Koch, "Insensitive High Explosives: III. Nitroguanidine – Synthesis – Structure – Spectroscopy – Sensitiveness," *Propellants, Explosives, Pyrotechnics*, vol. 44, no. 3, pp. 267-292, 2019.
- [7] R. Simkins and G. Williams, "592. The nitration of guanidine in sulphuric acid. Part I. The reversible conversion of guanidine nitrate into nitroguanidine," *Chemical Society*, no. 0, pp. 3086-3094, 1952.

6. Annex 1 - Methyl-3-Nitrobenzoate Preparation Procedure

Before Nitration
MB - light turquoise
MA - Clear.

Reaction Procedure

ALL HANDLING OF ACIDS IS TO BE CARRIED OUT IN A FUME CUPBOARD (FC).

Label glassware appropriately throughout the practical. *MB*

1. In a recirculation fume cupboard, weight out 2.7g of methyl benzoate into a 25cm³ conical flask using a Pasteur pipette.
2. In the ducted fume cupboard, measure out 5cm³ of concentrated sulfuric acid using a 10cm³ measuring cylinder, add to the methyl benzoate.
3. Swirl the flask gently to mix and cool the mixture by placing the conical flask in ice.
4. In a separate 5cm³ conical flask, prepare the nitrating mixture. Using a 10cm³ measuring cylinder, measure 2cm³ of conc. sulfuric acid and transfer to the conical flask labelled mixed acid. *MA*
5. To this add 2cm³ of concentrated nitric acid, you can use the same measuring cylinder to measure both acids.
6. Cool the mixed acids to 5°C by placing the conical flask in ice.

Turn the water bath on. During the nitration process make a note of any colour changes.

7. When the methyl benzoate mixture reaches 5°C add the nitrating mixture drop by drop to the solution of methyl benzoate using a pipette, ensuring the nitrating mixture does not get into the rubber teat.
8. Stir the mixture with a glass rod keeping the temperature below 10 °C. Allow the mixture to cool to 5 °C between additions.
9. When all the nitrating agent is added, leave the mixture to stand at room temperature for 15 minutes. This will be a very slow process for the first half of the mixed acid addition which will take ~1hr (due to the exothermic nature of the reaction) until equilibration when addition generates a lot less heat and addition is much faster.
10. During the 15-minute waiting period weigh out ~25g of crushed ice and place in a 100cm³ beaker.
11. Pour the reaction mixture from the conical flask onto the ice, stir until all the ice has melted and crystalline methyl-3 nitrobenzoate has formed.

Recrystallisation Procedure

12. Move the filtration equipment from your bench into the ducted fume cupboard. Fit the Buchner funnel into a Buchner flask and clamp it to prevent it falling over. Place the filter paper in the Buchner funnel and damp with a little chilled, distilled water. Connect the flask to the vacuum line with the tubing supplied.
13. Gently open the vacuum, pour the contents of the beaker into the filter funnel. Wash the crystals thoroughly with cold distilled water and remove excess water using the vacuum on high for 5 minutes.
14. Transfer the crystals to a 50 cm³ beaker.
15. Place 15 cm³ of ethanol into a small conical flask stand on the hot water bath to warm the ethanol to 50°C.

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Figure 5 - Methyl-3-nitrobenzoate Procedure Page 1

16. Place the beaker containing the sample on the water bath and pour small portions of the hot ethanol onto the crystals, stirring with a clean glass rod until the solid just dissolves.
17. Remove the beaker from the water bath and place onto a white ceramic tile. Leave the solution to cool to room temperature then immerse the beaker in ice water to allow the crystals of pure methyl nitrobenzoate to form.
18. Place the used Buchner funnel & flask at the back of the fume cupboard. Set up a clean Buchner funnel and flask, with a clean filter paper in the funnel. Damp the filter paper with a small portion of ethanol before turning on the vacuum. Filter the product under vacuum, dry the product by leaving the vacuum on for a few minutes. Transfer the product into a labelled, weighed sample bottle.

Give the sample to a technician who will dry it in a vacuum desiccator over lunchtime. After lunch reweigh bottle and contents to calculate amount of product obtained. Carry out melting point investigation.

Disposal of materials

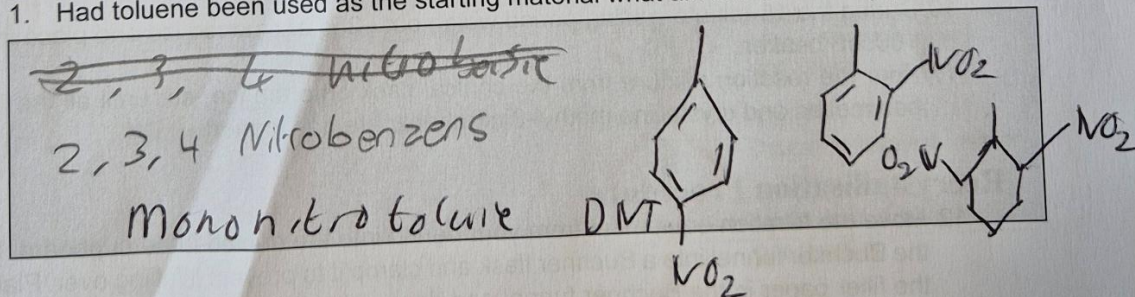
Spent acid from the nitration step must be placed at the back of the ducted FC for a technician to dispose of.

Residual solvent from the purification step must be decanted into the waste solvent residue bottle supplied.

Methyl-3- nitrobenzoate to be handed to a technician, for drying in the vacuum desiccator.

Questions

1. Had toluene been used as the starting material what are the three likely products?



2. Why keep the nitration mixture cool?

To stop run off reaction (controlling the reaction)

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Figure 6 - Methyl 3-nitrobenzoate Procedure Page 2

7. Annex 2 – Nitroguanidine Preparation Procedure

Reaction Procedure

1. In the fume cupboard, **carefully** measure out 5cm^3 of concentrated sulphuric acid using the measuring cylinder. Pour into a 50cm^3 beaker and place into the ice on the bench, taking care not to spill any acid. Using the thermometer wait for the temperature to fall below 5°C .
2. While the acid is cooling, weigh out 4 grams of guanidine nitrate into the weighing bottle.
3. When the acid has cooled, add small portions of guanidine nitrate with stirring to break up any solid lumps, ensuring that the temperature does not exceed 10°C .
4. When all the solid has been added, allow the mixture to stand for 2-3 minutes. Meanwhile place a filter paper into a Buchner funnel and damp it with a little distilled water. Clamp the Buchner flask, to prevent it falling over, and then fit the funnel to the flask using a rubber collar. Connect the flask to the vacuum line using the thick rubber hose.
5. After 2-3 minutes, pour out the mixture into a second 50cm^3 beaker containing 30cm^3 of water with a little ice and mix well with the glass rod. Ensure the product has fully precipitated by repeatedly pouring between the beakers.
6. Open the vacuum up and pour the contents of the beaker slowly into the funnel. Use a spatula to remove as much of your product from the beaker as possible.
7. Wash the crude product with a little cooled distilled water, then remove the water by vacuum filtration.

Recrystallisation Procedure

1. Transfer the crude product into a 150cm^3 beaker. Add hot distilled water until the solid just dissolves, with stirring and heating on the boiling water bath.
2. When **all** the product has been dissolved remove the beaker from the heat, allow it to cool to room temperature, then place the beaker in the ice. Crystals of the product will begin to form as the solution cools.
3. Clean the Buchner flask and funnel and place a clean filter paper into the funnel.
4. When recrystallisation is complete filter the product under vacuum. Wash the material with a little cool distilled water and dry the product by maintaining the vacuum in the filter apparatus.
5. Transfer the partially dried product into a weighed labelled bottle.
6. Give your product to a member of staff, who will dry it under vacuum for the next practical class.
7. When the material is completely dried (next practical class) reweigh the bottle with its contents to calculate the amount of product obtained.

Disposal of materials

Diluted acid residues are to be washed down a fume cupboard sink.
Bottled nitroguanidine is to be handed to a technician for disposal.