

Laboratory-Scale Nitration of Methyl Benzoate and Guanidine Nitrate: Synthesis, Yield Analysis
and Relevance to Energetic Materials.

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I. Abstract

Methyl-3-nitrobenzoate was prepared by nitration of methyl benzoate with a mixed nitric–sulfuric acid system. Nitroguanidine was prepared from guanidine nitrate in concentrated sulfuric acid. Procedures in the Cranfield instruction pack were followed. Methyl-3-nitrobenzoate was purified by recrystallisation from ethanol; both products were dried in a vacuum desiccator and weighed. From 2.694 g of methyl benzoate an 80.0 % yield of methyl-3-nitrobenzoate was obtained. From 4 g of guanidine nitrate a 68.4 % yield of nitroguanidine was obtained. Mechanisms, roles of reagents, relevance to ordnance, munitions and explosives (OME) and major sources of experimental error are discussed.

II. Table of Tables

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1. Purpose

The experiment was carried out to prepare methyl-3-nitrobenzoate and nitroguanidine on a small scale, to calculate percentage yields using the equations in the Cranfield instruction pack (Appendix A), and to relate the nitration chemistry to energetic-material synthesis used in OME.

2. Hypothesis

It was expected that nitration of methyl benzoate in a cold mixed nitric–sulfuric acid medium would give predominantly methyl-3-nitrobenzoate because the ester group is deactivating and meta-directing [1]. It was also expected that guanidine nitrate, when treated with cold concentrated sulfuric acid and then hydrolysed, would be converted to nitroguanidine [2]. Yields below 100 % were anticipated due to mechanical loss of product, incomplete conversion and minor side reactions if temperature control were imperfect.

3. Variables

3.1. Independent variables:

- Reaction temperature during addition of the mixed acid to methyl benzoate.
- Reaction temperature during addition of guanidine nitrate to concentrated sulfuric acid.
- Reaction time before quenching (methyl-3-nitrobenzoate) or before hydrolysis (nitroguanidine).
- Volume of ethanol used during recrystallisation of methyl-3-nitrobenzoate.

3.2. Dependent variables:

- Mass of methyl-3-nitrobenzoate obtained.
- Mass of nitroguanidine obtained.
- Percentage yield of each product, calculated from the measured masses and the equations in the Cranfield instruction pack.
- Physical appearance of the products (colour, crystal form).

3.3. Controlled variables:

- Identity and concentration of reagents (concentrated HNO_3 , concentrated H_2SO_4 , guanidine nitrate, ethanol).
- Stoichiometric ratios and volumes specified in the Cranfield instruction pack.
- Use of an ice bath for all strongly exothermic stages.
- Use of vacuum filtration and vacuum desiccation for drying solid products.
- Use of clean, labelled glassware for weighing and product storage.

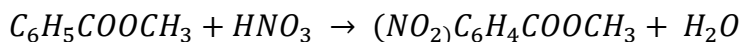
4. Theory

In the mixed acid, nitric acid is protonated and dehydrated by sulfuric acid to generate the nitronium ion:



The nitronium ion acts as an electrophile in electrophilic aromatic substitution [1]. Attack of NO_2^+ on the benzene ring of methyl benzoate forms a σ -complex, which then loses a proton to restore aromaticity [3]. The $-\text{COOCH}_3$ group is strongly electron withdrawing

and directs substitution to the meta position, so methyl-3-nitrobenzoate is produced as the major isomer:



The nitration mixture is kept cool to control the rate of NO_2^+ formation, limit over-nitration and oxidation and prevent a runaway exotherm [4].

For nitroguanidine, guanidine nitrate ($CH_6N_4O_3$) is dissolved in cold concentrated sulfuric acid. In this highly acidic and dehydrating medium, protonation, rearrangement and N-nitration occur, converting the guanidinium salt into the nitramine nitroguanidine ($CH_4N_4O_2$) with loss of water [5]:



The mechanism centres on formation of an $-N-NO_2$ group. Low temperature is necessary to prevent decomposition of intermediates and of nitroguanidine itself [1].

Concentrated sulfuric acid therefore acts as both strong acid and dehydrating agent in both experiments. Concentrated nitric acid provides the nitro group in the aromatic nitration. Ethanol is used as recrystallisation solvent because methyl-3-nitrobenzoate is soluble in hot ethanol but sparingly soluble in cold ethanol–water mixtures, allowing purification by crystallisation on cooling. Ice and water are used to quench the reactions, precipitate products and remove heat [6].

These methods are important to OME because aromatic nitration provides the primary industrial route for introducing nitro groups onto aromatic rings and thereby enabling the large-scale synthesis of high-energy nitroaromatic explosives such as TNT, DNT and

TATB. While nitroguanidine is itself a widely used energetic material in triple-base propellants and insensitive munition formulations [7].

5. Observations and Data

Procedures in the Cranfield instruction pack (Appendix A) were followed. Methyl benzoate appeared as a light tangerine liquid; the mixed acid was clear. After quenching onto ice, a cloudy suspension containing solid was observed. Following recrystallisation from hot ethanol and cooling, an off-white crystalline product was collected and dried under vacuum.

Nitroguanidine was obtained as a fine white to off-white crystalline, “fluffy” solid after dilution of the sulfuric-acid mixture into ice-water, filtration, washing and drying.

5.1. Methyl-3-nitrobenzoate

Quantity	Value (g)
Mass of methyl benzoate	2.694
Mass of labelled glass bottle	8.639
Mass of bottle + dried sample	11.5036
Mass of methyl-3-nitrobenzoate	2.8646

Table 1 - Methyl-3-nitrobenzoate Results

The theoretical yield was calculated using the Following expression:

$$\text{theoretical yield} = \text{mass of methyl benzoate} \times \frac{M_r(\text{methyl} - 3 - \text{Nitrobenzoate})}{M_r(\text{methyl Benzoate})}$$

so that

$$\text{theoretical yield} = 2.694\text{g} \times \frac{181.1}{136.1} = 3.58\text{g}$$

The actual yield corresponded to the isolated product mass:

$$\text{Actual Yield} = 11.5036 - 8.639 = 2.8646\text{g}$$

The percentage yield was then calculated as:

$$\% \text{yield} = \frac{\text{Actual yield}}{\text{Theoretical Yield}} \times 100 = \frac{2.8646}{3.58} \times 100 = 80.0\%$$

5.2. Nitroguanidine

Quantity	Value (g)
Mass of labelled bottle N	92.09
Mass of bottle N + dried nitroguanidine	94.424
Mass of nitroguanidine	2.334

Table 2 – Nitroguanidine Results

Using the yield expression for 4g guanidine nitrate:

$$\% \text{yield} = \frac{\text{Mass of NQ}}{\text{Mass of Guanidine Nitrate}} \times \frac{\text{Molar Mass Guanidine Nitrate}}{\text{Molar Mass Nitroguanidine}} \times 100$$

the nitroguanidine yield was calculated as:

$$\% \text{yield} = \frac{2.334}{4} \times \frac{122}{104} \times 100 = 68.4\%$$

6. Results and Discussion

The theoretical yield for methyl-3-nitrobenzoate represented the maximum product mass expected if all of the methyl benzoate had reacted completely with no losses or side reactions [8]. The actual yield was smaller because some material was inevitably lost during transfers, filtration and recrystallisation, and because a small fraction of the

starting material was likely to remain unreacted or to form minor by-products. These kinetic and mechanical limitations meant that the experimental yield approached, but did not reach, the theoretical value [9].

The 80.0 % yield indicates that the nitration procedure in the Cranfield instruction pack operated efficiently. The formation of a crystalline solid after recrystallisation is consistent with production of a single major aromatic nitro-ester, as predicted for meta-directed nitration of a deactivated ring. Yield could be improved further by more precise temperature control around 5 °C, slower addition of the mixed acid and use of the minimum effective volume of hot ethanol to reduce solubility losses [10].

The nitroguanidine yield of 68.4 % is lower, reflecting the greater sensitivity of that synthesis to conditions. Losses may have arisen from incomplete conversion of guanidine nitrate in the viscous sulfuric-acid medium, partial decomposition when local overheating occurred and loss of very fine crystals through the filter paper during washing. Improved stirring, closer temperature control and selection of a finer filter medium would be expected to raise the yield.

Impurity is particularly important for nitroguanidine. Residual sulphate, nitrate and moisture can remain after work-up and can lower decomposition temperature and alter burning behaviour. In practical OME manufacture, nitroguanidine is therefore further purified, carefully dried and then ground and classified to obtain a controlled particle-size distribution. Grinding is required because a defined size range improves packing density

and ensures more predictable burning rates, while oversized particles can give uneven burning and excessive fines can increase sensitivity and handling difficulties [10].

In both syntheses, the dominant experimental errors are judged to have arisen from temperature control, measurement uncertainty and mechanical product loss [10]. The strongly exothermic nature of both reactions means that small deviations in temperature can significantly change reaction rate and selectivity. Weighing and volume-measurement errors affect the calculated theoretical yield directly. Losses during transfer and filtration reduce the actual yield and cannot be fully avoided in small-scale glassware operations.

7. Conclusion

Methyl-3-nitrobenzoate was prepared from methyl benzoate by electrophilic aromatic nitration using a mixed nitric–sulfuric acid system and purified by recrystallisation from ethanol, giving an 80.0 % yield. Nitroguanidine was prepared from guanidine nitrate in concentrated sulfuric acid and isolated in 68.4 % yield. The difference between theoretical and actual yield for methyl-3-nitrobenzoate arose from incomplete conversion and unavoidable product losses during handling and purification. Both experiments illustrated the importance of temperature control, solvent choice and careful work-up when preparing energetic or energetic-related compounds relevant to OME.

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8. References

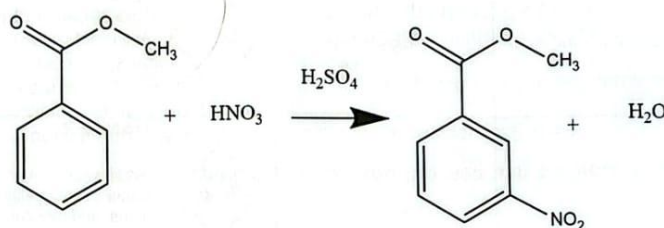
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9. Appendix A – Cranfield instruction pack

Experiment 1: Preparation of methyl-3-nitrobenzoate

Nitration is an important reaction in the manufacture of TNT, where the hydrogen atoms in a toluene molecule are replaced by nitro groups in a stepwise reaction. Benzene and benzene derivatives can undergo electrophilic substitution, where a hydrogen on the aromatic ring can be substituted with an electrophile, in this case a nitronium ion is generated by the mixed acid to produce a nitration reaction.



methyl benzoate + nitric acid $\longrightarrow$ methyl-3-nitrobenzoate + water

This reaction is very similar to that of the preparation of Di-nitrotoluene (DNT)

Hazards in the preparation of methyl -3-nitrobenzoate

All chemicals used in this experiment are harmful by inhalation, ingestion, and absorption through the skin. They must be handled in the fume cupboard and appropriate gloves worn. Nitric acid and sulfuric acid are highly corrosive and therefore very damaging to tissue. Any splashes must be washed off immediately with large amounts of water. Methyl benzoate is irritating to eyes, skin, and respiratory tract. Wash the affected areas with water. Remove to fresh air away from contaminated area for respiratory irritation. Ethanol is a potential irritant which causes drowsiness and impaired perception.

You will have been given a lab coat, safety glasses and be wearing appropriate clothing i.e., no open toes shoes or sandals. Feet covered with robust material. No shorts or skirts but legs covered to protect against possible splashes of conc. acid. Appropriate gloves can be found at the end of the bench. No eating (including chewing gum) or drinking in the laboratory. Listen carefully to the induction & follow the lab script.

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.

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. — MB
5. To this add 2cm³ of concentrated nitric acid, you can use the same measuring cylinder to measure both acids. — MA
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.

Label	Identity	GHS Hazard Symbols
Methyl benzoate	$C_6H_5COOCH_3$ (l)	 WARNING H302 Harmful if swallowed.  H361d Suspected of damaging the unborn child.
Conc. Sulphuric acid	H_2SO_4 (aq)	 DANGER H314 Causes severe skin burns, and eye damage.
Conc. Nitric acid	HNO_3 (aq)	 DANGER H314 Causes severe skin burns, and eye irritation.  H290 May intensify fire.  H331 Toxic if inhaled.
Ethanol	C_2H_5OH (l)	 DANGER H225 Highly flammable liquid and vapour  H319 Causes serious eye irritation.
Methyl-3-nitrobenzoate	$(NO_2)C_6H_4COOCH_3$ (s)	 WARNING Currently Pure methyl -3 - nitrobenzoate is not classified as hazardous. If contaminated with methyl benzoate then Harmful if swallowed. May cause skin irritation and serious eye irritation. Suspected of damaging unborn child.

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 solids just dissolve.
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, 3, 4 Nitrobenzene~~
2, 3, 4 Nitrobenzenes

2. Why keep the nitration mixture cool?

To stop run off reaction (controlling the reaction)

3. Why is ethanol used in recrystallisation?

next to 3 nitro benzoic acid is soluble

4. Calculate the yield?

5. How could the yield be improved?

- slower, cooler, precision

6. Describe and draw the stages of electrophilic substitution.

Observations

1/200 g of 10% solution, no milk
 Function of Vacuum - to speed up drying
 process.
 After 120 min with brown color

Results

Mass of labelled glass bottle	~~2.558~~ 8.639g
Mass of labelled glass bottle + dried sample	
Mass of Methyl 3-nitrobenzoate	
Actual yield	2.5

Mass of Methyl benzoate	2.694
Mr Methyl benzoate (C ₈ H ₈ O ₂)	
Mr Methyl 3-nitrobenzoate (C ₈ H ₇ NO ₄)	
Theoretical yield	
Percentage Yield	

$$\text{Theoretical yield} = \text{Mass of methyl benzoate} \times \frac{\text{Mr (methyl 3-nitrobenzoate)}}{\text{Mr (methyl benzoate)}}$$

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Melting point:

No Methyl benzoate
 as it is not present
 in actual.

$$\text{Actual yield} = \text{Mass of methyl benzoate} \times \text{Mr (Methyl 3-Nitrobenzoate)}$$