INSTRUCTOR'S INFORMATION

Nitrating Acetanilide or Methyl Benzoate: Electrophilic Aromatic Substitution

EQUIPMENT

General

apparatus, melting point
aspirators, with trap
balance, 0.001-g
tubes, capillary, melting point

Individual

bath, sand*, or hot plate
beaker, 50-mL
beaker, 400-mL†
clamp, utility
cylinder, graduated, 10-mL
cylinder, graduated, 50-mL
flask, Erlenmeyer, 25-mL
flask, Erlenmeyer, 125-mL
flask, filter, 125-mL
funnel, Büchner, 7.5-cm, with adapter
microspatula
paper, filter, 7.5-cm
pen, marking
3 pipets, Pasteur, with latex bulb
3 pipets, 1-mL, with rubber bulb
rod, stirring, glass
stand, support
2 test tubes, 15 × 125-mm

*electric heating well with heat controller
†ice bath

REAGENTS

(Required for 10 students performing *one* nitration. Reagent amounts include 30% spillage allowance.)

6.5 g acetanilide
65 mL 95% ethanol (for methyl nitrobenzoate)
130 mL 95% ethanol (for nitroacetanilide)
ice
6.5 mL methyl benzoate
6.5 mL concentrated nitric acid
20 mL concentrated sulfuric acid
water, distilled or deionized

PREPARATIONS

None

CHEMICAL HANDLING

Note: The information presented under **CHEMICAL HANDLING** may not conform to the latest Federal and state regulations because the regulations may have changed. Consult the appropriate agency for current information.

Specific information listed here concerning each of the chemicals used in this experiment should be compared to the contents of the corresponding MSDS.

Spillage Cleanup (for ***small*** amounts of liquids and solids in the stockroom)

1. Acetanilide: Sweep up and package for transfer to a chemical landfill.
Or, dispose of by method recommended by local regulations.

2. Ethanol: [***Caution:*** Flammable.] Mop up and pour into drain, diluting with a large amount of running water.
Or, dispose of by method recommended by local regulations.

3. Methyl benzoate: Mop up and package for transfer to a chemical incinerator.
Or, dispose of by method recommended by local regulations.

4. Nitric acid: Cover with powdered sodium hydrogen carbonate ($NaHCO_3$) until no more reaction occurs. Sweep up. Place in a glass container and carefully add water. Dissolve the material completely. Pour the neutralized solution into drain with a large amount of running water. Pour a solution of 5% $NaHCO_3$ over the original spill site. Mop up with paper towels. Dispose of in trash.

5. Sulfuric acid: See **4.** Nitric acid.

Collection Containers (for each work station servicing 10 students)

"Recovered Nitroacetanilide"
"Recovered Methyl Nitrobenzoate"
"Recovered 95% Ethanol"

Disposal

1. Recovered nitroacetanilide: Package for transfer to a chemical landfill.

Or, dispose of by method recommended by local regulations.

2. Recovered methyl nitrobenzoate: Package for transfer to a chemical incinerator.

Or, dispose of by method recommended by local regulations.

3. Recovered ethanol: Recycle by distilling.

Or, see **2.** Recovered methyl nitrobenzoate.

Hazard Alert

1. Acetanilide [*Registry of Toxic Effects of Chemical Substances (**RTECS**)*: 8 vols., U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, U.S. Government Printing Office: Washington, DC, 1987, #AD7350000]: Toxic and irritant. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

2. Ethanol (***RTECS#*** KQ6300000): Flammable and irritant. Prevent eye, skin, and clothing contact. Avoid inhaling the vapors and ingesting the compound.

3. Methyl benzoate (***RTECS#*** DH3850000): Irritant. Prevent eye, skin, and clothing contact. Avoid inhaling the vapors and ingesting the compound.

4. Nitric acid (***RTECS#*** QU5775000): Toxic and oxidizer. Can cause severe burns. Prevent eye, skin, clothing, and combustible material contact. Avoid inhaling the vapors and ingesting the compound.

5. Methyl 3-nitrobenzoate (no ***RTECS#***): Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

6. 4'-Nitroacetanilide (***RTECS#*** AE5075000): Irritant. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

7. Sulfuric acid (***RTECS#*** WS5600000): Toxic and oxidizer. Can cause severe burns. Prevent eye, skin, clothing, and combustible material contact. Avoid inhaling vapor and ingesting the compound.

COMMENTS ON THE EXPERIMENT

Estimated bench time is 3 hr.

1. Acids can be safely dispensed from bottle-top dispensers. If micropipets are used, warn students not to pull the acids too rapidly into the pipets. The acids can attack the seals on the pipets.

2. Make certain nitric and sulfuric acids are ***cold*** before mixing.

3. You may wish to use magnetic stirrers for the 30–45 min nitration in Part 3.

4. You may wish to have half the students nitrate acetanilide and half nitrate methyl benzoate. They can compare regiochemistry results.

5. You may choose to photocopy the attached data sheet for student use.

REPRESENTATIVE STUDENT DATA

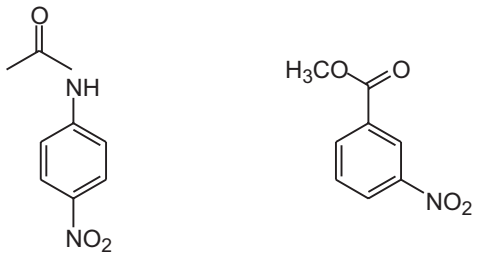
Student yields range from 40–70%. Most students have no difficulty identifying the regiochemistry of their products.

ANSWERS TO POST-LABORATORY QUESTIONS

1. (a) and (b) Results will vary.

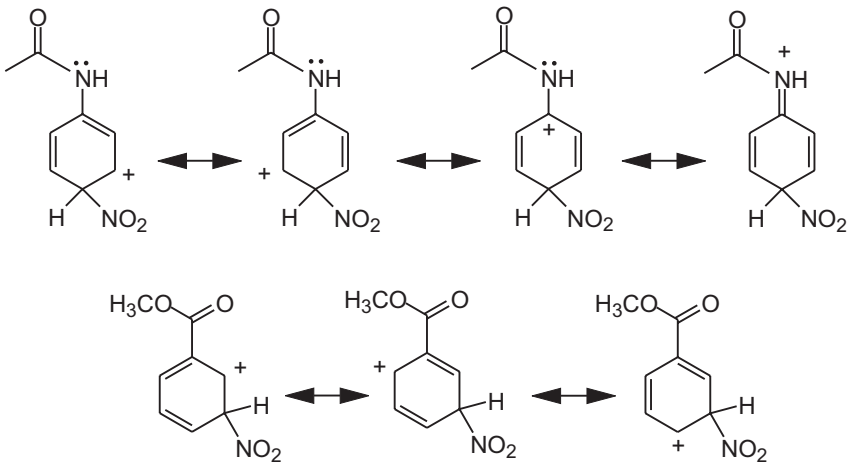
(c) product regiochemistry: acetanilide: *para*; methyl benzoate: *meta*

(d)



para- nitroacetanilide *meta*- methyl nitrobenzoate

2.



3. Nitro groups are deactivators. Each additional nitro group deactivates the ring, making electrophilic substitution more difficult.

ANSWERS TO PRE-LABORATORY ASSIGNMENT

1. A precaution to take when using concentrated acids is to prevent eye, skin, and clothing contact because concentrated acids can cause severe burns.

2. (a) Electrophilic aromatic substitution will occur at these positions for the following compounds.

bromobenzene	*ortho-para*	toluene	*ortho-para*
nitrobenzene	*meta*	phenol	*ortho-para*
benzoic acid	*meta*	benzaldehyde	*meta*

(b) Phenol is the most reactive because –OH is a strong activator.

(c) Nitrobenzene is the least reactive because $-NO_2$ is a strong deactivator.

3. The theoretical yields for the mononitration of acetanilide and methyl benzoate:

AA = acetanilide NAA = nitroacetanilide

$$\text{g NAA} = 0.5\ \text{g AA}\left(\frac{1\text{mol AA}}{135.17\ \text{g}}\right)\left(\frac{180.16\ \text{g}}{1\text{mol NAA}}\right) = 0.67\ \text{g}$$

MB = methyl benzoate MNB = methyl nitrobenzoate

$$\text{g MNB} = 0.55\ \text{g MB}\left(\frac{1\text{mol MB}}{136.15\ \text{g}}\right)\left(\frac{181.13\ \text{g}}{1\text{mol MNB}}\right) = 0.73\ \text{g}$$

name _____ section _____ date _____

Data Sheet

Electrophilic Aromatic Substitution

		acetanilide	*methyl benzoate*
amount of aromatic reactant used,	g	_____	_____
	moles	_____	_____
product obtained,	g	_____	_____
	moles	_____	_____
product theoretical yield,	g	_____	_____
	moles	_____	_____

product yield, % _____

Write the equation for reaction.

Product Characterization

	nitroacetanilide	*methyl nitrobenzoate*
melting point, °C		
product regiochemistry		