Nitration (Lab X-A)

Background Reading

McMurry, J., Organic Chemistry, 8e 571-2 or 7e 551-2 (nitronium ion),
8e 588-9 or 7e 568-9 (electrophilic aromatic substitution).
Zanger, M. and McKee, J.R. Small Scale Syntheses. pp 26-8 (recrystallization),
and 197-8 (aromatic subst'n).
Zubrick, J. W. The Organic Chem Lab Survival Manual. Ch 13: Recrystallization.

Keywords

Electrophilic Aromatic Substitution, Meta-Director, Deactivator,
Nitronium Ion, and Recrystallization

Compound, Reaction, and Yield Data

- Include balanced overall reaction and detailed reaction mechanism.
- Note product crystals' appearance in your observations.
- Determine yield % using density of methyl benzoate to convert volume to mass, and 15.8 M for concentrated HNO_3 to convert volume to moles.
- Compare melting point with tabulated values.

Infrared Spectral Data

Note the exact location of following IR absorptions on your product's spectrum:

- Aromatic ring: 3090/ 3960 (C−H), 2000 −1800 weak, and 1600 / 1450 medium
- Carbonyl (C=O): 1700 strong
- Nitro ($-NO_2$): 1536 medium

Procedure

1. Place a 50-ml beaker with a stir bar in an ice-water bath, and clamp the beaker to a stand. Add 3 ml of concentrated H_2SO_4.

   Caution – Concentrated H_2SO_4 solutions are corrosive and cause acid burns. Use gloves and avoid all contact with skin and eyes.

2. Cool to 5.0 ^{o}C while stirring.
   Then, slowly and carefully add 1.2 ml of methyl benzoate.

3. Put a small test tube in a 150-ml beaker of ice-water. Clamp beaker to a stand.
   Add 1 ml of concentrated H_2SO_4, and then add 1 ml of concentrated HNO_3.
   Add the nitric acid to the sulfuric acid, not the reverse.
   This prevents loss of NO_2^{+1} (nitronium ion) by conversion to NO_2NO_3 and N_2O_5.
   Mix drop-wise (slowly and carefully) with a micropipette and cool to 20 ^{o}C.

   Caution – Concentrated H_2SO_4 and HNO_3 solutions
   are corrosive and cause acid burns.
   Use gloves and avoid all contact with skin and eyes.

4. Add the nitration mixture drop-wise (slowly and carefully)
   to the methyl benzoate solution using a micropipette.
   Ensure temperature does not rise above 30 ^{o}C.

5. Remove reaction mixture from cooling bath and stir mixture for 15 minutes.

6. Quench reaction by pouring the mixture over 1" of ice,
   mixing them together, into a 100-ml beaker. Scrape the
   remaining solids from the reaction beaker with a spatula.

7. Place two 50-ml (or smaller) beakers in an ice-water bath.
   Cool 15 ml of DI water in one beaker
   and 7 ml of 95% ethanol in the other.
   Allow to cool for at least 5 minutes.
   Save these to use for washing product crystals.

   Collect crude product (solid) by vacuum filtration using
   a 55-mm Büchner funnel and a 250-ml vacuum flask.
   If product clumps, gently break up the clumps with a glass
   stirring rod to release any trapped acid.

   Wash product crystals with two 6-ml portions of cold DI water,
   then with two 3-ml portions of cold ethanol (from ice-water bath).

   Place all used solutions in the appropriately labeled waste jar.

8. Purify product by recrystallization as follows.
   Add crude product (solid) to 20 ml of 50% ethanol in a clamped 50-ml Erlenmeyer flask.
   Place in a warm water bath that is at least 50 ^{o}C, and stir as necessary to dissolve.
   Do not allow bath temperature to go above 60 ^{o}C, because the product can
   irreversibly form an insoluble "oil" if it approaches its melting point (79 ^{o}C).
   Add up to 10-ml more 50% ethanol to dissolve the solid if necessary.
   Insoluble impurities can be removed by decanting the liquid to another flask.

(step 8 continued)
Cool solution in an ice-water bath to crystallize.
If product does not crystallize during cooling,
add up to 5-ml of 95% ethanol.

Collect purified product by vacuum filtration using
a 55-mm Büchner funnel and 250-ml vacuum flask.
Weigh filter paper first. Scrape the remaining
solids from the reaction beaker with a spatula.

Place all used solutions in the appropriately labeled waste jar.

9. Dry in 45 ^{o}C oven for 15 minutes. Then, obtain yield and melting point.
Do two trials for MP. (2nd trial should be slower and more accurate.)

Dissolve 0.1 g of solid in CH_2Cl_2 in a small test tube.
Use only just enough liquid to dissolve the product.
Obtain IR spectrum using this solution on a salt plate.

Place product in the appropriately labeled waste jar.

Post-Lab Questions

1. Why is methyl benzoate a deactivator? Why is it a meta director?
See electronic effects of substituents and substituent category 4
in the chapter 16 notes.

2. Why would 0 ^{o}C ice in step 6 absorb heat better than 0 ^{o}C water?
What is the heat (or enthalpy) of fusion for water in kJ per mole?

3. What is the side product of the reaction that forms the nitronium ion,
and what happens to that side-product during the nitration reaction?
See nitration in the chapter 16 notes.

4. What other products can form from the reactant and product if the
temperature in step 4 is > 30 ^{o}C? Provide structures and systematic
names. See trisubstituted benzenes in the chapter 16 notes, as well
as Table 16.1 in McMurry.

5. Why doesn't sulfonation occur? What is required for sulfonation?
See sulfonation in the chapter 16 notes.