INSTRUCTOR'S INFORMATION

Reducing Benzil Using Sodium Borohydride

EQUIPMENT

General

apparatus, melting point
balance, 0.001-g
oven, 100-°C

TLC

hood, fume
lamp, UV
scissors

IR Spectroscopy

paper, IR chart
pens, plotter
press, pellet
spectrophotometer, infrared

Individual

Microscale

bath, sand*
beaker, 50-mL†
cotton
cylinder, graduated, 10-mL
2 flasks, Erlenmeyer, 10-mL
flask, filter, 25-mL, with vacuum tubing
funnel, Hirsch, with adapter
microspatula
paper, filter, for Hirsch funnel
2 pipets, Pasteur, with latex bulb
pipet, 1-mL, with rubber bulb
test tube, 13 × 100-mm
thermometer, –10 to 260 °C

*sand in crystallizing dish on electric hot plate or sand in electric heating well with heat controller
†for ice bath

Semi-Microscale

beaker, 500-mL*
chip, boiling
cylinder, graduated, 10-mL
cylinder, graduated, 50-mL
2 flasks, Erlenmeyer, 125-mL
flask, filter, 125-mL, with vacuum tubing
funnel, Büchner, 5-cm, with adapter
hot plate
paper, filter, 5-cm, for Büchner funnel
spatula, metal
test tube, 18 × 150-mm
thermometer, –10 to 260 °C
watch glass, 90-mm

*for ice bath

Identifying the Product

cylinder, graduated, 10-mL
jar, 4-oz screw cap* †
microburner*
microspatula
pen, marking
pencil*
2 pipets, Pasteur, with latex bulb
plate, silica gel, 3 × 6-cm*
ruler, mm*
4 tubes, melting point capillary
2 tubes, capillary, open-end*
3 vials, 3-mL*

*for TLC
†or 250-mL beaker with plastic wrap for cover

REAGENTS

(Required for 10 students. Reagent amounts include 30% spillage allowance.)

Microscale

1.3 g benzil
13 mL 95% ethanol
0.3 g sodium borohydride ***(Note: Must be fresh from unopened, newly purchased bottle.)***
ice

Semi-microscale

13 g benzil
130 mL 95% ethanol
2.6 g sodium borohydride ***(Note: Must be fresh from unopened, newly purchased bottle.)***
ice

Mixture melting point determinations

65 mg (±)-benzoin
65 mg *meso*-hydrobenzoin

TLC

29 mL ethyl acetate
52 mL *n*-hexane
25 mg (±)-benzoin
25 mg *meso*-hydrobenzoin

IR spectroscopy

1.3 g potassium bromide*
*spectroscopic grade, kept in an oven at 100 °C

PREPARATIONS

1. Benzoin sample: Weigh 5 mg (±)-benzoin and place it into a vial as a demonstration quantity for Identifying the Product, Part 2, on page 10 in the experiment module.

2. Benzoin standard for TLC: Weigh 1–2 mg (±)-benzoin and place it into a vial as a demonstration quantity for Identifying the Product, Part 3, on page 10. Or, weigh 1–2 mg (±)-benzoin and place it into a vial. Add 2–3 drops of ethyl acetate to dissolve the sample.

3. *meso*-Hydrobenzoin standard for TLC: Weigh 1–2 mg *meso*-hydrobenzoin and place it into a vial as a demonstration quantity for Identifying the Product, Part 3, on page 10. Or, weigh 1–2 mg *meso*-hydrobenzoin and place it into a vial. Add 2–3 drops of ethyl acetate to dissolve the sample.

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. Benzil: Sweep up and place in a container for transfer to a chemical incinerator.

2. (±)-Benzoin: See **1.** Benzil.

3. Ethanol: [***Caution:*** Flammable.] If local regulations allow, mop up and pour into the drain, diluting with a large amount of running water.

4. Ethyl acetate: Carefully mop up and place in “Recovered Ethyl Acetate–Hexane Solvents” container.

5. *n*-Hexane: See **4.** Ethyl acetate.

6. *meso*-Hydrobenzoin: See **1.** Benzil.

7. Potassium bromide: Sweep up and transfer to “Recovered KBr Pellets” container.

8. Sodium borohydride: See **1.** Benzil.

Collection Containers (for each work station servicing 10 students)

You will need the following appropriately labeled collection containers:

“Recovered Ethyl Acetate–Hexane Solvent”
“Recovered Benzil Reduction Products”
“Recovered Filtrate”
“Discarded Capillary Tubes”
“Used TLC Plates”
“Recovered KBr Pellets”

Disposal

Because of the wide variety of local and state regulations, consult your safety officer for the procedures needed to dispose of the waste generated in this experiment. Consult local authorities for current regulations. Wear appropriate OSHA approved respirator, chemical-resistant gloves, rubber boots, and other protective clothing.

1. Discarded capillary tubes: Depending on local regulations, dispose of as trash.

Or, package for transfer to a chemical landfill.

2. Recovered benzil reduction products: Package for transfer to a chemical landfill.

3. Recovered ethyl acetate–hexane solvent: Recycle by drying and distilling.

Or, package for transfer to a chemical incinerator.

4. Recovered filtrate: If local regulations allow, pour into the drain, diluting with a large amount of running water.

5. Recovered KBr pellets: Package for transfer to a chemical landfill.

Or, dispose of by method recommended by local regulations.

6. Used TLC plates: See **1.** Discarded Capillary Tubes.

Hazard Alert

1. Benzil [*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, D. C., 1987, #DD1925000]: Irritant. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

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

3. Ethyl Acetate (***RTECS#*** AH5425000): Flammable and irritant. Fire hazard. Prevent eye, skin and clothing contact. Avoid inhaling the vapors and ingesting the compound.

4. *n*-Hexane (***RTECS#*** MN9275000): Flammable and irritant. Fire hazard. Prevent eye, skin and clothing contact. Avoid inhaling the vapors and ingesting the compound.

5. Potassium bromide (***RTECS#*** TS7650000): Irritant and hygroscopic. Prevent eye, skin and clothing contact. Avoid ingesting the compound.

6. Sodium borohydride (***RTECS#*** ED3325000): Flammable and corrosive. Fire hazard. Prevent contact with acids. Prevent eye, skin and clothing contact. Avoid ingesting the compound.

COMMENTS ON THE EXPERIMENT

Estimated bench time is 2.5–3 hr.

1. The success of this experiment depends upon the use of *fresh* $NaBH_4$ from an unopened, newly purchased bottle.

2. Yellow benzil converts to white *meso*-hydrobenzoin within 2–3 min after adding $NaBH_4$. Students will enjoy observing the color change.

3. If the microscale product is kept on the Hirsch funnel with the water aspirator on high for 4–5 min, oven drying is usually unnecessary. If the product mass is not constant, dry the product in a 100-°C oven for 10 min.

4. If product crystals are damp, measured melting points will be low, which could lead to incorrect identification using the flowchart in the student module, Figure 4.

5. The isolated *meso*-hydrobenzoin is very pure. It melts at 137–139 °C. Careful work can produce a 70% yield on both the micro- and semi-microscales.

6. Reagent grade ligroin, bp 60–80 °C, may be substituted for reagent grade *n*-hexane in the TLC analysis.

7. Addition of 20 mL of 80-°C water does not cause the reaction solution to become cloudy in the semi-microscale reaction, as in the microscale reaction. Allowing the solution to cool, however, will cause the *meso*-hydrobenzoin to precipitate.

8. You may wish to divide the students into three groups and have one group identify the product by mixture melting point, another by TLC, and the third by IR spectroscopy. The three groups can then compare results.

9. If time allows, students can identify the product using any combination of the three techniques of mixture melting point, TLC, and IR spectroscopy.

10. Plastic-backed 20 × 20-cm TLC plates with a fluorescent indicator are available from Kodak. Using scissors, trim to 2.5 × 6-cm to maximize the use of 20 × 20-cm TLC plates.

11. (+)-Benzoin or (–)-benzoin may be substituted for (±)-benzoin in the mixture melting point, TLC, and IR analyses.

12. Familiarity with mixture melting points, recrystallization, TLC, and IR are assumed. If your students are not familiar with a technique, you may need to provide demonstrations and additional background information. These techniques are presented in the following modules in the MLPC series: TECH 701, *Measuring the Melting Points of Compounds and Mixtures*; TECH 703, *Purifying Acetanilide by Recrystallization;* TECH 707, *Separating a Mixture of Biphenyl, Benzhydrol, and Benzophenone by Thin-Layer Chromatography*; and TECH 710, *Identifying an Unknown Compound by Infrared Spectroscopy*.

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

REPRESENTATIVE STUDENT DATA

Percent yields range from 35–100% with an average of 67%. Typical R_fs are 0.25 for *meso*-hydrobenzoin and 0.5 for (±)-benzoin. R_fs vary with different silica gel preparations, but comparison to standards is consistent. Student TLC data confirm the product as *meso*-hydrobenzoin. Student IR spectra show no carbonyl absorption at 1609 cm^{-1}, consistent with *meso*-hydrobenzoin, but not consistent with (±)-benzoin.

ANSWERS TO POST-LABORATORY QUESTIONS

1. Reduction of benzil to form (±)-benzoin requires reduction of only one of the two carbonyl groups. Therefore, one $NaBH_4$ molecule can reduce four benzil molecules.

$$0.100\ \text{g benzil}\left(\frac{1\ \text{mol benzil}}{210.22\ \text{g benzil}}\right)\left(\frac{1\ \text{mol NaBH}_4}{4\ \text{mol benzil}}\right)\left(\frac{37.85\ \text{g NaBH}_4}{1\ \text{mol NaBH}_4}\right)\left(\frac{1000\ \text{mg}}{1\ \text{g}}\right) = 4.5\ \text{mg NaBH}_4$$

2. Reducing benzil to hydrobenzoin requires reducing both carbonyl groups. Therefore, one $NaBH_4$ molecule can reduce only two benzil molecules.

$$0.100\ \text{g NaBH}_4\left(\frac{1\ \text{mol NaBH}_4}{37.85\ \text{g NaBH}_4}\right)\left(\frac{2\ \text{mol benzil}}{1\ \text{mol NaBH}_4}\right)\left(\frac{210.22\ \text{g}}{1\ \text{mol benzil}}\right) = 1.11\ \text{g benzil}$$

3. (a) The melting point of the product is 137 °C, thus eliminating (±)-hydrobenzoin as a possibility.

(b) Mixture melting point confirms that the product is *meso*-hydrobenzoin. When the product is mixed with (±)-benzoin, the melting point lowers to 114–124 °C. When the product is mixed with a standard sample of *meso*-hydrobenzoin, the melting point remains at 137 °C.

(c) Thin-layer chromatography also confirms that the product is *meso*-hydrobenzoin. The product has an R_f of approximately 0.25 on Kodak silica gel plates using *n*-hexane: EtOAc/2:1 (v/v) as the solvent, matching the R_f of pure *meso*-hydrobenzoin. (±)-Benzoin has an R_f of approximately 0.5 under these conditions.

(d) Because both carbonyl groups have been reduced in the conversion of benzoin to *meso*-hydrobenzoin, the IR spectrum of the product shows an OH stretch at 3350–3425 cm^{-1} but *no carbonyl stretch*. (±)-Benzoin shows both an OH stretch at 3425 cm^{-1} and a carbonyl stretch at 1609 cm^{-1}.

4. (a) Because the product is *meso*-hydrobenzoin, one $NaBH_4$ molecule can reduce only two benzil molecules.

$$\text{benzil used, mol} = 0.100\text{ g benzil}\left(\frac{1\text{ mol}}{210.22\text{ g benzil}}\right) = 4.8\times10^{-4}\text{ mol}$$

$$\text{NaBH}_4\text{ used, mol} = 0.02\text{ g NaBH}_4\left(\frac{1\text{ mol}}{37.85\text{ g NaBH}_4}\right) = 5.3\times10^{-4}\text{ mol}$$

$$\text{NaBH}_4\text{ needed, mol} = 4.8\times10^{-4}\text{ mol benzil}\left(\frac{1\text{ mol NaBH}_4}{2\text{ mol benzil}}\right) = 2.4\times10^{-4}\text{ mol}$$

Therefore, benzil is the limiting reagent.

(b) The theoretical amount of *meso*-hydrobenzoin is 4.8×10^{-4} mol because one molecule of benzil produces one molecule of product.

$$4.8\times10^{-4}\text{ mol}\left(\frac{214.27\text{ g }\textit{meso}\text{-hydrobenzoin}}{1\text{ mol}}\right)\left(\frac{1000\text{ mg}}{1\text{ g}}\right) = 102.8\text{ mg }\textit{meso}\text{-hydrobenzoin}$$

(c) Answers will vary depending on the actual yield.

$$\text{percent yield, \%} = \left(\frac{\text{actual yield}}{102.8\text{ mg}}\right)(100\%)$$

5. The IR spectrum of benzil shows a strong carbonyl absorption at 1680 cm^{-1} and an aromatic CH stretch at 3100 cm^{-1}. *Meso*-hydrobenzoin shows no carbonyl absorption and a strong OH stretch at 3350–3450 cm^{-1}. In addition to two small aromatic CH stretches at around 3100 cm^{-1}, an aliphatic CH stretch appears at 2950 cm^{-1}.

ANSWERS TO PRE-LABORATORY ASSIGNMENT

1. (a) In a reduction reaction, either hydrogen is added to or oxygen is removed from an organic molecule. The reduction of the keto groups of benzil to yield *meso*-hydrobenzoin is a typical example.

(b) Enantiomers are non-superimposable mirror-image stereoisomers, such as (+)-benzoin and (–)-benzoin.

(c) A racemic mixture is a mixture of two enantiomers, such as (±)-hydrobenzoin.

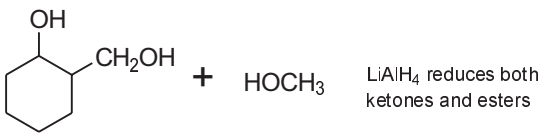
(d) Diastereomers are stereoisomers that are not mirror images, such as (+)-hydrobenzoin and *meso*-hydrobenzoin.

(e) A *meso*-compound is one that is optically inactive even though it contains chiral centers. It contains a plane of symmetry and is superimposable on its mirror image. An example is *meso*-hydrobenzoin.

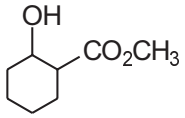
2. (a) $(CH_3)_2CHCH_2CH_2CH_2OH$

(b) no reaction; $NaBH_4$ does not reduce esters

(c)



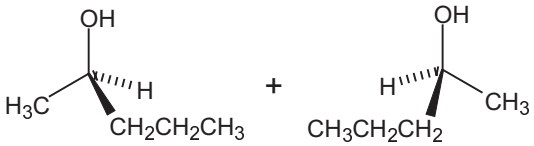
(d)



$NaBH_4$ reduces the keto group, but not the ester

3. Because *m*-acetylbenzaldehyde has two groups that $NaBH_4$ can reduce, the four H^- from a single $NaBH_4$ molecule can reduce only two *m*-acetylbenzaldehyde molecules.

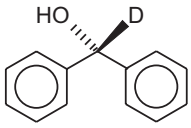
4.



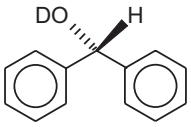
(R) -2-pentanol *(S)* -2-pentanol

Both compounds are produced in the reaction because attack can occur at either face of the starting ketone.

5. (a)



(b)



6. (a) diastereomers

(b) identical

(c) enantiomers

(d) different compounds, not isomeric

name _____ section _____ date _____

Data Sheet

Reducing Benzil

	g	*mol*
amount of benzil used	_____	_____
amount of sodium borohydride used	_____	_____
product obtained	_____	_____
product theoretical yield	_____	_____

product yield, % _____

Write the equation for the reaction.

Identifying the Product

	product	*(±)-benzoin*	*meso*-hydrobenzoin
melting point, °C			
melting point with (±)-benzoin, °C			
melting point with *meso*-hydrobenzoin, °C			
R_f			

Name of product _____