INSTRUCTOR'S INFORMATION

Synthesis of *trans*-9-(2-Phenylethenyl)anthracene: A Wittig Reaction

EQUIPMENT

General

apparatus, melting point
balance, 0.001-g
chips, boiling
evaporator, rotary*
gloves, polyethylene
holder, sample, IR
hood, fume
labels
lamp, UV
paper, filter, to fit funnel
press, KBr
spectrometer, nuclear magnetic resonance
spectrophotometer, infrared

*if available

Individual

Semi-Microscale

beaker, 50-mL
2 beakers, 100-mL
beaker, 250-mL*
2 clamps, utility
condenser, with tubing
cylinder, graduated, 10-mL
dropper, medicine
flask, Erlenmeyer, 25-mL
flask, filter, 250-mL, with vacuum tubing
flask, round-bottom, 25-mL
funnel, Büchner, with adapter
funnel, separatory, 125-mL, with stopper
head, distilling
hot plate
microspatula
2 stands, support
stir bar, magnetic
stirrer, magnetic
vial, product
watch glass

*for ice bath and for hot-water bath

Microscale

2 beakers, 10-mL
beaker, 250-mL*
clamp, utility
cylinder, graduated, 10-mL
dropper, medicine
flask, Erlenmeyer, 25-mL
flask, filter, 25-mL,with vacuum tubing
funnel, Hirsch, with adapter
hot plate
microspatula
pipet, 1.0-mL†
2 pipets, Pasteur, with latex bulb
stand, support
stir bar, magnetic
stirrer, magnetic
tube, centrifuge, 10-mL, with screw cap
tubing, vacuum
vial, conical, 5.0-mL
vial, product
watch glass

*for ice bath and for hot-water bath
†or adjustable micropipet

Product Characterization

Melting Point

tubes, capillary melting point

Thin-Layer Chromatography

cylinder, graduated, 10-mL
2 jars, 4-oz, screw-cap*
microburner and tubing
paper, filter, 12-cm, cut to fit the developing chamber
pencil
pipet, transfer, 0.1-mL
plate, TLC, 2 × 9-cm silica gel, with fluorescent indicator
ruler, cm
tubes, capillary, open-ended
vial, conical, 1.0-mL

*or 400-mL beakers, with aluminum foil covers

Infrared Analysis

press, pellet, KBr*
mortar and pestle, agate†
plates, NaCl or AgCl, with sample holder†

*for KBr pellets
†for mull

NMR Analysis

pipet, Pasteur, with latex bulb
tube, sample, NMR
vial, conical, 3.0-mL

REAGENTS

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

Wittig Synthesis	*Semi-Microscale*	*Microscale*
9-anthraldehyde	6.8 g	1.4 g
benzyltriphenylphosphonium chloride	13 g	2.7 g
calcium chloride, anhydrous	13 g	3.9 g
dichloromethane	230 mL	40 mL
ice		
2-propanol	260 mL	65 mL
50% aqueous sodium hydroxide	17 mL	3.5 mL

Product Characterization

13 mL *deutero*-chloroform
3 mL mineral oil*
1.3 g potassium bromide†
130 mL toluene

*for mull
†for KBr pellets

PREPARATIONS

1. 50% Aqueous sodium hydroxide (25 mL): Dissolve 12.5 g NaOH (MM: 40 g/mol) in 20 mL distilled or deionized water. Cool to room temperature. Add enough water to make 25 mL of solution. Store in a plastic bottle.

2. TLC plates: Silica gel GF can be used to prepare TLC plates before the laboratory time. Or, cut sheets of commercially prepared TLC plates to 2 × 9-cm pieces. Activate the plates by heating them in a drying oven at 100 °C for 15 min.

3. 9-Anthraldehyde TLC spotting solution: Place 10 mg of 9-anthraldehyde in a 2-mL vial. Dissolve in 1 mL of toluene.

4. Potassium bromide, spectroscopic grade: Heat in an oven at 100 °C for 30 min. Either keep in oven or transfer to a desiccator.

5. Potassium bromide sample: Weigh 100 mg of KBr in a 1-mL screw-cap vial, labeled "estimate of 100 mg of KBr"**.**

6. *trans*-9-(2-Phenylethenyl)anthracene sample: Weigh 2 mg of *trans*-9-(2-phenylethenyl)anthracene in a 1-mL screw-cap vial, labeled "estimate of 2 mg of product"**.**

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. 9-Anthraldehyde: Sweep up. Package for disposal in a chemical landfill.

2. Benzyltriphenylphosphonium chloride: See **1.** 9-Anthraldehyde.

3. Calcium chloride: Sweep up. Dispose of in trash if local regulations permit.

Or, add to "Recovered $CaCl_2$" container.

4. *deutero*-Chloroform: Adsorb on vermiculite. Package for transfer to a chemical incinerator.

5. Dichloromethane: See **4.** *deutero*-Chloroform.

6. Potassium bromide: Sweep up. If local regulations allow, discard in trash.

Or, see **1.** 9-Anthraldehyde.

7. 2-Propanol: [***Caution:*** Flammable.] See **4.** *deutero*-Chloroform.

8. Sodium hydroxide solution: Cover with powdered sodium hydrogen carbonate ($NaHCO_3$) until no more reaction occurs. Sweep up. Place in glass container and carefully add water. Dissolve the material completely. Pour into the drain, diluting 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.

9. Toluene: [***Caution:*** Flammable.] See **4.** *deutero*-Chloroform.

Collection Containers

You will need the following appropriately labeled containers:

"Recovered Aqueous Layer"
"Recovered Dichloromethane"
"Recovered 2-Propanol"
"Recovered $CaCl_2$"
"Recovered Toluene"
"Recovered KBr Pellets"
"Recovered d-Chloroform"
"Used TLC Plates"
"Discarded Capillary Tubes"

Disposal

> ***Note:*** Because of the wide variety of local and state regulations governing the types of reaction mixtures generated in this experiment, consult local authorities for current regulations.

1. Discarded capillary tubes: Place discarded glass materials in the laboratory "Broken Glass" container.

2. Recovered aqueous layer: Dilute with water and pour into the drain, diluting with a large amount of running water.

3. Recovered $CaCl_2$: Depending on local regulations, dispose of as trash.

4. Recovered *d*-chloroform: Package for transfer to a chemical incinerator.

5. Recovered dichloromethane: Recycle the dichloromethane by drying and distilling.

Or, package for transfer to a chemical incinerator.

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

Or, dispose of by method recommended by local regulations.

7. Recovered 2-propanol: See **5.** Recovered dichloromethane.

8. Recovered toluene: See **5.** Recovered dichloromethane.

9. Used TLC plates: Depending on local regulations, dispose of as trash.

Hazard Alert

1. 9-Anthraldehyde: Irritant. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

2. Benzyltriphenylphosphonium chloride: Irritant and hygroscopic. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

3. Calcium chloride, anhydrous [*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, #EV9800000]: Irritant and hygroscopic. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

4. *deutero*-Chloroform (***RTECS#*** FS9100000]: Toxic and suspected carcinogen. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

5. Dichloromethane (***RTECS#*** PA8050000): Toxic and irritant. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

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

7. 2-Propanol (***RTECS#*** NT8050000): Flammable and irritant. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

8. Sodium hydroxide (***RTECS#*** WB4900000): Toxic, corrosive, and hygroscopic. Prevent eye, skin, and clothing contact. Avoid inhaling and ingesting the compound.

9. Toluene (***RTECS#*** XS5250000): Flammable and toxic. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

DEMONSTRATIONS

1. Demonstrate any instrumental techniques with which your students are not familiar.

2. Demonstrate the amount of product needed for TLC, IR, and NMR analyses.

COMMENTS ON THE EXPERIMENT

Estimated bench time is 3 hr.

1. Depending on the quality of your reagents, you may see a precipitate from the reaction. If such a precipitate occurs, use a cotton plug to filter the precipitate or emulsions will form during extraction.

2. Phase separation paper is an alternative to using drying agents such as $CaCl_2$. Phase separation paper is available from a variety of vendors.

3. Emphasize the need to prevent overheating of the sample during the removal of the solvent.

4. Depending on the frequency of use, you may need to remind students of techniques associated with TLC, IR, NMR, melting point measurement, recrystallization, extraction, distillation, and drying agents.

5. The R_fs of *trans*-9-(2-phenylethenyl)anthracene and 9-anthraldehyde in toluene are 0.92 and 0.50, respectively. Some variation will occur with R_fs depending on the moisture content of the silica gel.

6. Make certain all micropipets are prepared and all burners are removed ***before*** any flammable eluents are opened in the laboratory.

7. A variety of containers can serve as developing chambers. The simplest arrangement is a 250- or 400-mL beaker covered tightly with aluminum foil or plastic wrap. A wide-mouth Mason jar can be used. Wide-mouth 4-oz screw-cap jars are suitable for microscope slide-size TLC plates. Before using plastic wrap, make certain the eluent will not dissolve it.

8. Residual toluene may mask fluorescence. To avoid this problem, dry plates completely before UV visualization. Drying time is 15–20 min.

9. Interpret the IR spectrum with caution. The *trans*-CH=CH- group has a strong absorption band at 962 cm^{-1}. The mono-substituted benzene absorption at 680 cm^{-1} could be mistaken for the *cis*-CH=CH- group.

10. The NMR spectrum of the product clearly shows the *trans* isomer. The vinylic protons produce the expected pair or doublets of an AX system: one at δ = 6.82 ppm, J = 17 Hz; the other at δ = 7.82 ppm, J = 17 Hz.

11. You may wish to photocopy the attached data sheet for student use.

REPRESENTATIVE STUDENT DATA

A typical student yield is 50–70% for semi-microscale and 40–65% for microscale. Melting points range 120–129 °C. R_fs range 0.81–0.87 and 0.39–0.46 for product and 9-anthraldehyde, respectively.

ANSWERS TO POST-LABORATORY QUESTIONS

1. Results will vary. See **Representative Student Data**.

2. Results will vary slightly. The R_fs of *trans*-9-(2-phenylethenyl)anthracene and 9-anthraldehyde in toluene are 0.92 and 0.50, respectively. See **Representative Student Data**.

3. The melting point and R_f match reported values for the *trans* isomer. The melting point of the *cis* isomer has not been reported.

4. Most notably, 9-anthraldehyde has characteristic aldehyde absorptions at 2820 and 2720 cm^{-1} and at 1700 cm^{-1}, while the product does not.

5. In the NMR spectrum, the vinylic protons of the *trans* isomer produce the expected pair or doublets of an AX system: one at δ = 6.82 ppm, J = 17 Hz; the other at δ = 7.82 ppm, J = 17 Hz. The deciding factor pointing to the *trans* isomer is the coupling constant. In the IR spectrum, the *trans*-CH=CH– group has a strong absorption band at 962 cm^{-1}. The mono-substituted benzene absorption at 680 cm^{-1} could be mistaken for the *cis*-CH=CH– group. Therefore, great care should be taken in interpreting this spectrum.

ANSWERS TO PRE-LABORATORY ASSIGNMENT

1. (a) Dichloromethane is toxic and irritating. Avoid getting dichloromethane in your eyes, and on your skin and clothing. Use it in a fume hood. Do not inhale fumes and ingest dichloromethane.

(b) Avoid contact with eyes, skin, or clothing. Use gloves. Do not inhale and ingest this compound.

(c) Avoid contact with eyes, skin, or clothing. Do not use near flames or other heat sources. Do not inhale fumes and ingest this compound.

2. The dehydrohalogenation reaction may yield multiple isomers. The Wittig reaction results in a single alkene.

3. (a) The molar ratio of the reactants is one to one, so either reagent is limiting.

*t*PEA = *trans*-9-(2-phenylethenyl)anthracene; AA = 9-anthraldehyde; BTPC = benzyltriphenylphosphonium chloride

semi-microscale

$$\left(\frac{0.520\ \text{g AA}}{206.24\ \text{g/mol}}\right) = 0.0025\ \text{mol AA} \quad \left(\frac{0.980\ \text{g BTPC}}{388.88\ \text{g/mol}}\right) = 0.0025\ \text{mol BTPC}$$

microscale

$$\left(\frac{0.110\ \text{g AA}}{206.24\ \text{g/mol}}\right) = 0.0005\ \text{mol AA} \quad \left(\frac{0.210\ \text{g BTPC}}{388.88\ \text{g/mol}}\right) = 0.0005\ \text{mol BTPC}$$

(b)

semi-microscale

$$t\text{PEA, g} = \left(\frac{0.520\text{ g AA}}{206.24\text{ g/mol}}\right)\left(\frac{280.4\text{ g/mol}}{1\text{mol }t\text{PEA}}\right) = 0.707\text{ g}$$

microscale

$$t\text{PEA, g} = \left(\frac{0.110\text{ g AA}}{206.24\text{ g/mol}}\right)\left(\frac{280.4\text{ g/mol}}{1\text{mol }t\text{PEA}}\right) = 0.150\text{ g}$$

4. (a) $CH_3CH_2CH(CH_3)CHO$ and $[Ph_3PCH_2CH_3]^+ Cl^-$
or $[CH_3CH_2CH(CH_3)CH_2PPh_3]^+ Cl^-$ and CH_3CHO

(b) $(CH_3)_2C{=}O$ and $[Ph_3PCH_2C_6H_5]^+ Cl^-$
or $[Ph_3PCH(CH_3)_2]^+ Cl^-$ and C_6H_5CHO

name _____ section _____ date _____

Data Sheet

Wittig Reaction

	mL	*g*	*mol*
amount of 9-anthraldehyde used	_____	_____	_____
amount of benzyltriphenylphosphonium chloride used	_____	_____	_____
product obtained		_____	_____
product theoretical yield		_____	_____

product percent yield, % _____

Write the equation for the reaction.

Product Characterization

	9-anthraldehyde	*trans-9-(2-phenylethenyl) anthracene*
melting point		
R_f		
major IR bands, cm^{-1}		
NMR bands, ppm		