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

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PURPOSE OF THE EXPERIMENT

Synthesize *trans*-9-(2-phenylethenyl)anthracene using a Wittig reaction. Characterize the product by melting point, thin-layer chromatography, infrared spectroscopy, and nuclear magnetic resonance spectroscopy.

EXPERIMENTAL OPTIONS

BACKGROUND REQUIRED

You should be familiar with techniques for drying organic solvents and measuring melting points. You should be familiar with the techniques for extraction, distillation, recrystallization, and vacuum filtration. You should know how to speed the evaporation of microscale quantities of solvent using air or nitrogen. You should be familiar with thin-layer chromatography (TLC), infrared spectroscopy (IR), and nuclear magnetic resonance spectroscopy (NMR).

BACKGROUND INFORMATION

Chemical reactions involving organic molecules can be classified into three very broad categories: molecular rearrangement, elimination, and addition. Although alkenes are commonly formed from *elimination* reactions, such as dehydration of alcohols and dehydrohalogenation of alkyl halides, these reactions usually result in a mixture of structural isomers. The Wittig reaction is often preferred as a method of synthesizing alkenes because of its high level of **regioselectivity**, which is the tendency of a reaction to form predominantly one isomer from a single reactant. The Wittig reaction allows the chemist to choose the precise location of the newly formed bond.

The Wittig reaction is an *addition* reaction. It generates an alkene from the reaction of a carbonyl compound with a carbon-containing phosphorus reagent known as an ylide, which is made from a phosphonium halide. The phosphonium halide is generated from the nucleophilic substitution reaction of a primary or secondary alkyl halide and triphenylphosphine, Ph_3P. Ph_3P is a good nucleophile and a relatively weak base. Therefore, the potentially competing elimination reaction

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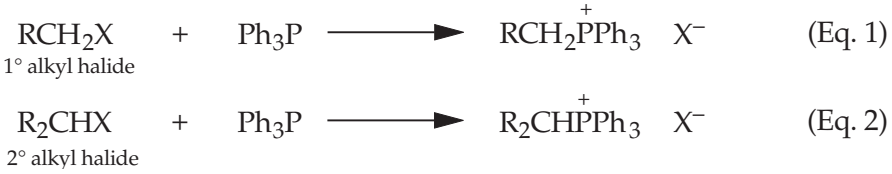
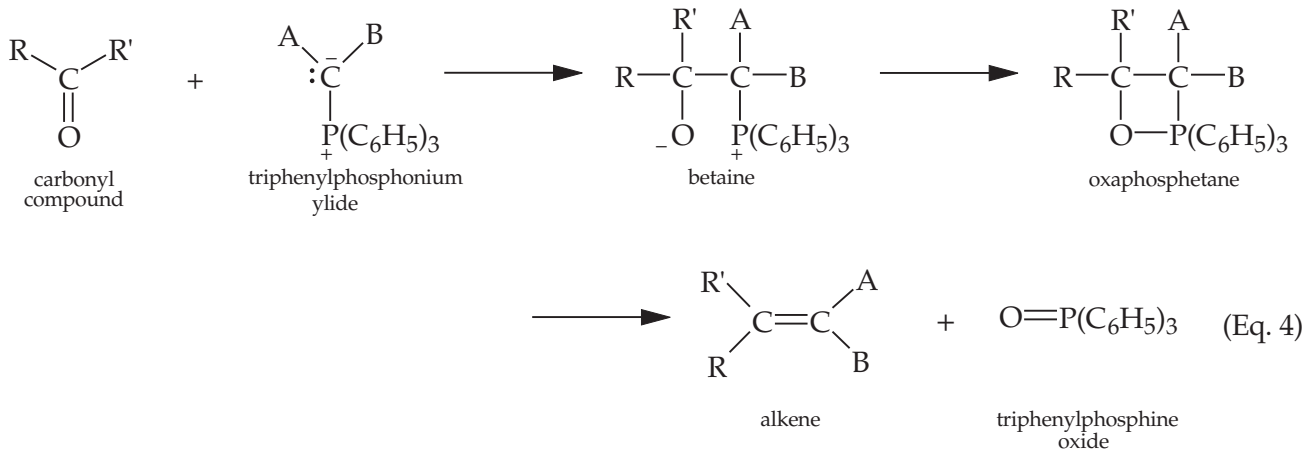
does not occur. The substitution products are phosphonium salts, as shown in Equations 1 and 2.



The phosphonium salt must have phosphorus attached to a carbon containing at least one hydrogen atom. This hydrogen atom is moderately acidic and can be extracted in the presence of a strong base. Typically, alkyl lithium compounds or metal hydrides are used as the strong base. In this experiment, however, a concentrated solution of aqueous sodium hydroxide will be used.

The product resulting from the reaction of the phosphonium halide with a strong base is called an **ylide**. An ylide is a neutral molecule, which, among its atoms, has two adjacent atoms that have opposite charges. The two charged atoms are the phosphorus from the phosphine and the carbon from the alkyl halide, as shown in Equation 3.

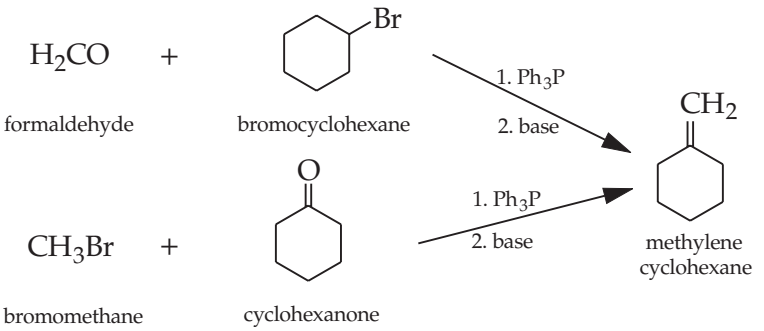
This carbon group attached to the phosphorus has carbanionic character and acts as a nucleophile toward carbonyl groups. The general mechanism of the reaction is shown in Equation 4.



The mechanism is still under investigation. The controversy lies in whether the oxaphosphetane intermediate is formed by a one-step concerted process or by a two-step process. Formation of the oxaphosphetane through a two-step process involves the initial formation of a dipolar intermediate known as a betaine. The betaine then reacts to form the oxaphosphetane. The oxaphosphetane is stable at –78 °C, but at room temperature, it decomposes to yield the alkene and triphenylphosphine oxide. The driving force for the decomposition of the oxaphosphetane is thought to be the formation of the strong phosphorus–oxygen bond of the phosphine oxide, a bond strength estimated to be at least 540 kJ/mol.

The Wittig reaction forms the carbon–carbon double bond between the carbonyl carbon and the carbon adjacent to the phosphorus atom in the ylide. For example, consider the formation of methylenecyclohex-

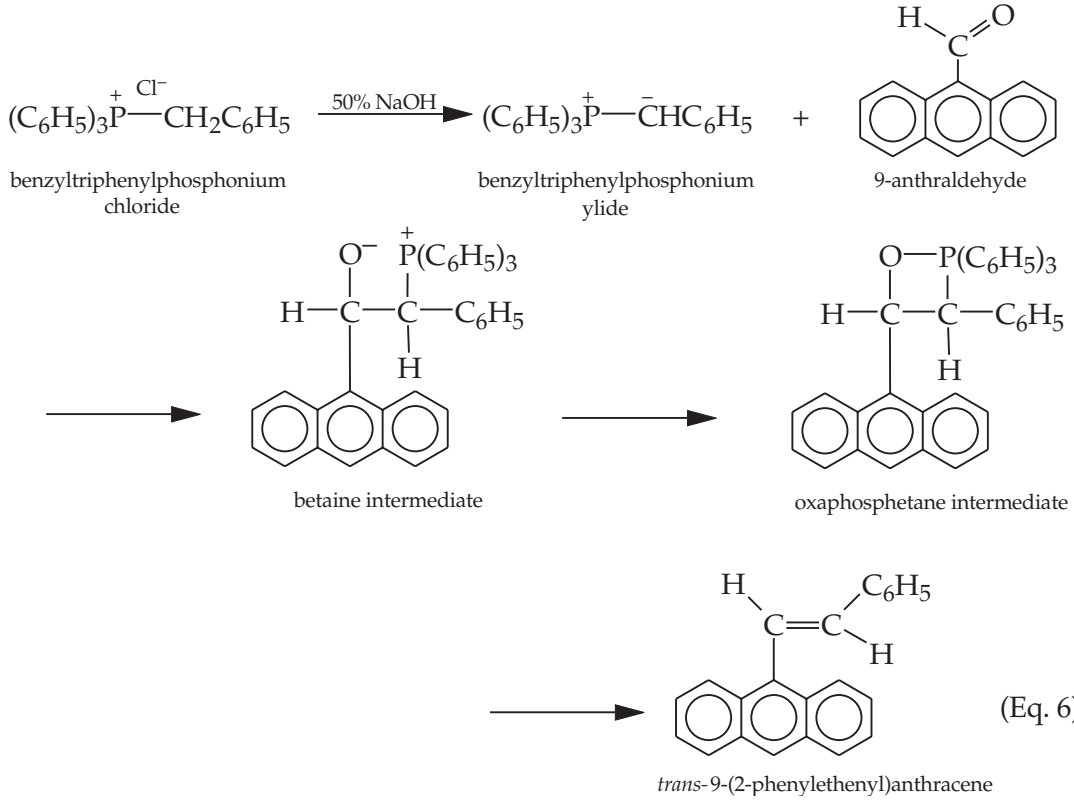
ane. The Wittig reaction could be conducted with formaldehyde and bromocyclohexane or with bromomethane and cyclohexanone, as shown in Equation 5.



(Eq. 5)

The synthetic route chosen will depend on the availability of the possible starting materials.

In this experiment, the alkene *trans*-9-(2-phenylethenyl)anthracene will be synthesized from 9-anthraldehyde and the ylide derived from triphenylbenzylphosphonium chloride. The ylide formation and the subsequent reaction are shown in Equation 6.



(Eq. 6)

Semi-Microscale Wittig Synthesis

Equipment

50-mL beaker	Büchner funnel, with adapter
2 beakers, 100-mL	condenser, with tubing
250-mL beaker*	distilling head
boiling chip	25-mL Erlenmeyer flask

250-mL filter flask, with vacuum tubing
filter paper
10-mL graduated cylinder
hot plate
magnetic stir bar
magnetic stirrer
medicine dropper
microspatula
product vial
25-mL round-bottom flask
125-mL separatory funnel
2 support stands
2 utility clamps
watch glass
*for ice bath and for hot-water bath

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*bp (°C)*	*mp (°C)*	*d (g/mL)*
9-anthraldehyde	0.520 g	206.24		104–105	
benzyltriphenyl-phosphonium chloride	0.980 g	388.88			
calcium chloride, anhydrous	1 g	110.99			
dichloromethane	18 mL	84.93	40		1.325
trans-9-(2-phenyl-ethenyl)anthracene*		280.4		130–132	
2-propanol	20 mL	60.10	82		0.785
50% sodium hydroxide	1.3 mL				

*product

Preview

- Dissolve benzyltriphenylphosphonium chloride and 9-anthraldehyde in dichloromethane
- Add 50% aqueous sodium hydroxide
- Stir the reaction mixture vigorously for 30 min
- Use a separatory funnel to separate the dichloromethane layer from the aqueous layer
- Extract the aqueous layer with additional dichloromethane
- Dry the combined dichloromethane layers over anhydrous calcium chloride
- Remove the solvent from the crude product
- Recrystallize the crude product from 2-propanol
- Dry and weigh the product

PROCEDURE

Chemical Alert

9-anthraldehyde—*irritant*

benzyltriphenylphosphonium chloride—*irritant and hygroscopic*

anhydrous calcium chloride—*irritant and hygroscopic*

dichloromethane—*toxic and irritant*

2-propanol—*flammable and irritant*
50% sodium hydroxide—*corrosive and toxic*

Caution: Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

1. Using a Wittig Reagent to Synthesize *trans*-9-(2-Phenylethenyl)anthracene

Caution: Benzyltriphenylphosphonium chloride and 9-anthraldehyde are irritating. Dichloromethane is toxic and irritating. Use a ***fume hood***.

50% Sodium hydroxide (NaOH) is corrosive and toxic. Wear gloves when using this solution. Prevent eye, skin, and clothing contact. Avoid inhaling and ingesting these compounds.

Weigh 0.980 g of benzyltriphenylphosphonium chloride and 0.520 g of 9-anthraldehyde. Place them into a 25-mL Erlenmeyer flask. Add 3 mL of dichloromethane. Place the flask on top of a magnetic stirrer and add a stir bar.

While the mixture is vigorously stirring, add 1.3 mL of 50% aqueous sodium hydroxide at a rate of 1 drop every 7 s. Vigorously stir the reaction mixture for an additional 30 min.

2. Isolating *trans*-9-(2-Phenylethenyl)anthracene

Caution: 2-Propanol is flammable and irritating. Keep away from flames or other heat sources. Anhydrous calcium chloride ($CaCl_2$) is irritating and hygroscopic. Prevent eye, skin, and clothing contact. Avoid inhaling and ingesting these compounds.

Transfer the reaction mixture from the Erlenmeyer flask to a 125-mL separatory funnel. Rinse the reaction flask with 10 mL of dichloromethane and transfer the rinse to the separatory funnel. Then rinse the reaction flask with 10 mL of distilled or deionized water and transfer the rinse to the separatory funnel.

Shake and vent the contents in the funnel. Allow the layers to separate. Drain the organic layer from the funnel into a 100-mL beaker labeled, "Organic Layer".

Add an additional 5 mL of dichloromethane to the aqueous layer in the funnel. Shake and vent the contents in the funnel. Drain the organic layer into the beaker containing the initial organic layer.

Dry the combined organic layers by adding up to 1 g of anhydrous $CaCl_2$ to the beaker. Cover the beaker with a watch glass and allow the solution to dry for 10 min. Decant the organic layer from the drying agent into a dry 25-mL round-bottom flask.

3. Removing the Dichloromethane [NOTE 1]

Using a Rotary Evaporator

Use a rotary evaporator to collect the dichloromethane from the product, as directed by your laboratory instructor.

Using Distillation

Set up a simple distillation apparatus in the ***fume hood***. Use the 25-mL round-bottom flask containing your product as the distilling flask. Add a boiling chip. Use a hot-water bath to distill the dichloromethane from the product. Collect the dichloromethane in a 50-mL beaker.

NOTE 1: Use the separation method designated by your laboratory instructor.

4. Purifying *trans*-9-(2-Phenylethenyl) anthracene

Add 20 mL of 2-propanol to a 100-mL beaker. Heat the 2-propanol to boiling using a hot plate or electric flask heater. Recrystallize the crude product from 2-propanol. Allow the flask to cool to room temperature. Then place the solution in an ice-water bath for 5–10 min.

Collect the product by vacuum filtration using a Büchner funnel. Continue the suction for 5 min to dry the product. Weigh the product and place it into a labeled product vial.

Proceed to the Characterizing the Product Section on page 8. Use the procedures designated by your laboratory instructor.

5. Cleaning Up

Use the labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

***Caution*:** Wash your hands with soap or detergent before leaving the laboratory.

Microscale Wittig Synthesis

Equipment

2 beakers, 10-mL	hot plate
250-mL beaker*	magnetic stir bar
10-mL centrifuge tube, with screw cap	magnetic stirrer
5-mL conical vial	medicine dropper
25-mL Erlenmeyer flask	microspatula
25-mL filter flask, with vacuum tubing	2 Pasteur pipets, with latex bulb
filter paper	1-mL pipet†
10-mL graduated cylinder	product vial
Hirsch funnel, with adapter	support stand
	utility clamp
	watch glass

*for ice bath and for hot-water bath

†or adjustable micropipet

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*bp (°C)*	*mp (°C)*	*d (g/mL)*
9-anthraldehyde	0.110 g	206.24		104–105	
benzyltriphenyl-phosphonium chloride	0.210 g	388.88			
calcium chloride, anhydrous	0.3 g	110.99			
dichloromethane	3.1 mL	84.93	40		1.325
trans-9-(2-phenyl-ethenyl)anthracene*		280.4		130–132	
2-propanol	5 mL	60.10	82		0.785
50% sodium hydroxide	0.26 mL				

*product

Preview

- Dissolve benzyltriphenylphosphonium chloride and 9-anthraldehyde in dichloromethane
- Add 50% aqueous sodium hydroxide
- Stir the reaction mixture vigorously for 30 min
- Separate the dichloromethane layer from the aqueous layer in a centrifuge tube
- Extract the aqueous layer with additional dichloromethane
- Dry the combined dicloromethane layers over anhydrous calcium chloride
- Remove the solvent from the crude product
- Recrystallize the crude product from 2-propanol
- Dry and weigh the product

PROCEDURE

Chemical Alert

9-anthraldehyde—*irritant*

benzyltriphenylphosphonium chloride—*irritant and hygroscopic*

anhydrous calcium chloride—*irritant and hygroscopic*

dichloromethane—*toxic and irritant*

2-propanol—*flammable and irritant*

50% sodium hydroxide—*corrosive and toxic*

Caution: Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

1. Using a Wittig Reagent to Synthesize *trans*-9-(2-Phenylethenyl)anthracene

Caution: Benzyltriphenylphosphonium chloride and 9-anthraldehyde are irritating. Dichloromethane is toxic and irritating. Use a ***fume hood***. Prevent eye, skin, and clothing contact. Avoid inhaling and ingesting these compounds.

50% Sodium hydroxide (NaOH) is corrosive and toxic. Wear gloves when using this solution. Prevent eye, skin, and clothing contact. Avoid inhaling and ingesting this compound.

Weigh 0.210 g of benzyltriphenylphosphonium chloride and 0.110 g of 9-anthraldehyde. Place them into a 5-mL conical vial. Add 0.6 mL of dichloromethane. Place the vial on top of a magnetic stirrer and add a stir bar. Clamp the vial in place for added stability.

While the mixture is vigorously stirring, add 0.26 mL of 50% aqueous sodium hydroxide at a rate of 1 drop every 7 s. Vigorously stir the reaction mixture for an additional 30 min.

2. Isolation and Purification of *trans*-9-(2-Phenylethenyl) anthracene

Transfer the reaction mixture from the vial to a 10-mL centrifuge tube. Rinse the reaction vial with 1.5 mL of dichloromethane and transfer the rinse to the centrifuge tube. Then rinse the reaction vial with 1.5 mL of distilled or deionized water and add the rinse to the centrifuge tube.

Screw the cap onto the centrifuge tube and shake it vigorously, venting the tube periodically. Allow the layers to separate. Using a Pasteur

pipet, transfer the organic layer from the centrifuge tube to a 10-mL beaker labeled, "Organic Layer".

Add an additional 1 mL of dichloromethane to the aqueous layer in the centrifuge tube. Shake and vent the contents in the tube. Transfer the organic layer to the beaker containing the initial organic layer.

Dry the combined organic layers by adding up to 0.3 g of anhydrous $CaCl_2$ to the beaker. Cover the beaker with a watch glass and allow the solution to dry for 10 min.

Decant the organic layer from the drying agent into a dry 10-mL beaker. Use a steam bath or a hot-water bath in a ***fume hood*** to carefully evaporate the dichloromethane from the crude product. Do not overheat the beaker and melt the crude product. Use a *gentle* stream of air or nitrogen to speed the evaporation process.

Add 5 mL of 2-propanol to a 25-mL Erlenmeyer flask. Heat the 2-propanol to boiling, using a hot plate or electric flask heater. Recrystallize the crude product from hot 2-propanol. Allow the flask to cool to room temperature. Then place the solution in an ice-water bath for 5–10 min.

Collect the product by vacuum filtration using a Hirsch funnel. Continue the suction for 5 min to dry the product. Weigh the product and place it into a labeled product vial.

Proceed to the Characterizing the Product Section. Use the procedures designated by your laboratory instructor.

3. Cleaning Up Use the labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

***Caution*:** Wash your hands with soap or detergent before leaving the laboratory.

Characterizing the Product

Equipment

Melting Point

melting point capillary tubes

Thin-Layer Chromatography

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

*or 400-mL beakers, with aluminum foil covers

Infrared Analysis

KBr pellet press*
NaCl or AgCl plates, with sample holder†

*for KBr pellets
†for mull

NMR Analysis

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

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*bp (°C)*	*mp (°C)*
9-anthraldehyde		206.24		104–105
deutero-chloroform	1 mL	120.39	60.9	
potassium bromide	100 mg			
toluene	10 mL	92.14	110.6	

Preview

- Measure the melting point of the product
- Prepare a thin-layer chromatogram and measure the product R_f
- Analyze the product using infrared spectroscopy
- Analyze the product using nuclear magnetic resonance spectroscopy

PROCEDURE

Chemical Alert

9-anthraldehyde—*irritant*

deutero-chloroform—*toxic and suspected carcinogen*

toluene—*flammable and toxic*

Caution: Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

1. Measuring Melting Point

Take a melting point of the product. Heat the melting point tube quickly to 110 °C, then slow the heating rate to 2 °C per min. Observe and record the temperature range over which the solid melts.

2. Using Thin-Layer Chromatography

Caution: Toluene is flammable and toxic. Do not use toluene near flames or other heat sources. ***Use toluene only when all students have prepared their micropipets and all flames have been extinguished.*** Use a ***fume hood.*** Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting toluene.

Prepare micropipets for spotting the TLC plate by drawing out open-ended capillary tubes.

Prepare a developing chamber using approximately 10 mL of toluene as the eluent.

Place 0.1-mL of toluene in a 1.0-mL conical vial. Add 1–2 mg of your product and mix to dissolve.

Using a *pencil*, lightly draw a line across the bottom of a TLC plate, 1 cm above the bottom. Carefully make two light hash marks on the line and label them as "starting material" and "product".

Caution: 9-Anthraldehyde is irritating. Prevent eye, skin, and clothing contact.

Spot 9-anthraldehyde, using the solution provided by your laboratory instructor, and the product, using the solution you prepared, on the plate. Place the plate into the developing chamber.

Develop the plate until the eluent front is approximately 1 cm from the top. Then remove the chromatogram from the chamber and *immediately* mark the eluent front with a pencil.

Caution: Ultraviolet radiation can cause severe damage to the eyes. Wear goggles. Do not look directly into the lamp.

Allow the eluent to evaporate under the ***fume hood***. Examine the chromatogram under the UV lamp and lightly circle the spots using a pencil.

Using a ruler, measure the distance to the eluent front and to the center of each spot. Record the values.

3. Using Infrared Spectroscopy

Caution: Potassium bromide (KBr) is irritating. Prevent eye, skin, and clothing contact. Avoid inhaling dust.

Prepare the sample for IR analysis following the instructions of your laboratory instructor. Obtain an IR spectrum of your sample.

4. Using Nuclear Magnetic Resonance Spectroscopy

Caution: *deutero*-Chloroform (*d*-chloroform) is toxic and a suspected carcinogen. Use gloves. Use a ***fume hood***. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

Obtain an NMR sample tube from your laboratory instructor. In a dry vial, place approximately 10 mg of product and 1 mL of *d*-chloroform. Swirl the vial until all of the solid has dissolved. Use a Pasteur pipet to transfer at least 0.600 mL of the solution to the NMR tube and cap the tube.

Follow the instructions of your laboratory instructor to obtain an NMR spectrum of your sample.

5. Cleaning Up

Use the labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

***Caution*:** Wash your hands with soap or detergent before leaving the laboratory.

Post-Laboratory Questions

1. Calculate the percent yield of product you obtained from this reaction.
2. Calculate R_fs for each spot on your chromatogram.
3. Using your melting point data and thin-layer chromatogram, what evidence allows you to conclude that your product is *trans*-9-(2-phenylethenyl)anthracene?
4. Compare the IR spectra for 9-anthraldehyde and that of your product. What evidence allows you to conclude that your product is *trans*-9-(2-phenylethenyl) anthracene?
5. Using your IR and NMR spectra, what evidence supports the synthesis of the *trans* isomer rather than the *cis* isomer?

NAME SECTION DATE

SYNT 721/Synthesis of trans-9-(2-Phenylethenyl) anthracene: A Wittig Reaction

Pre-Laboratory Assignment

1. What safety precautions must be observed when using
   (a) dichloromethane?

   (b) 50% aqueous sodium hydroxide?

   (c) toluene?

2. Briefly explain the advantage of a Wittig synthesis over the more common dehydrohalogenation reaction.

3. Using the data in the Reagents and Properties table,
   (a) identify which reactant is the limiting reagent in the reaction;

   (b) calculate the theoretical yield, in grams, of *trans*-9-(2-phenylethenyl)anthracene. Show your calculation here and in your laboratory notebook.

4. What combination of carbonyl compound and phosphorus ylide could you use to prepare the following alkenes?
   (a) $CH_3CH_2CH(CH_3)CH{=}CHCH_3$

   (b) $(CH_3)_2C{=}CHC_6H_5$

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