Experiment 7: Synthesis of an Alkyne from an Alkene

Part A: Synthesis of meso-stilbene dibromide
Part B: Synthesis of diphenylacetylene

Reading: Carey & Guiliano
Ch. 9 pgs 368-372

Note: This is exp #8 in the lab manual

Synthesis of an Alkyne from an Alkene

• This week's synthesis:

   step 1:

   step 2:

• Overall conversion (alkene to alkyne) difficult to achieve in a single step

Step 1: Bromination of Stilbene

- electrophilic addition of bromine to a double bond
- general reaction of alkenes
- occurs rapidly and with defined stereochemistry

• typically done with bromine (Br₂) - corrosive liquid!!
• We will use pyridinium hydrobromide perbromide (a.k.a. pyridinium tribromide)
  - orange solid
  - convenient source of Br₂ (generated in situ)

Step 1: Reaction Mechanism

Electrophilic Addition:

• Reaction is stereospecific
  - selective addition across double bond (relative orientation of groups on double bond carbons stays the same)
  - backside attack of bromide - S₈2 mechanism
Step 2: Dehydrobromination

- elimination of HBr in the presence of a strong base
- general reaction of organic halides
- also has specific stereochemical requirements
- can be used to form both alkynes (double elimination) or alkenes

Next Week (October 24 - October 28)

Experiment 7: Synthesis of an Alkyne from an Alkene

A. Synthesis of meso-dibromostilbene
   bromination of a double bond

B. Synthesis of diphenylacetylene
   dehydrobromination (double elimination of bromine)

DUE: Dehydration/GC Lab Report (exp 6)
Lab Reports are due at the beginning of your regular lab session

Reaction Mechanism

E2 elimination:

- dehydrohalogenation is concerted
  bond breaking and bond formation occur at the same time

Experimental Details - Step 1: Bromination

1. Combine reactants in an Erlenmeyer flask
dissolve E-stilbene in acetic acid (heat gently - 30-35°C)
   add pyridinium hydrobromide perbromide (pyridinium tribromide)
   add reagent all at once
   rinse vessel walls with a little acetic acid if necessary
2. Swirl to mix & continue heating (ca. 5 min)
crystals (product) will begin to separate almost immediately
3. Cool reaction vessel in cold water (no ice)
4. Collect product by vacuum filtration
5. Wash crystals sparingly with ice cold methanol; dry
crystals should be colorless
dry thoroughly under vacuum using your side arm test tube
6. Weigh product - will use to calculate the % yield
7. Save a small amount for TLC
   note: this product is the starting material for the next reaction
Experimental Details - Step 2: Dehydrobromination

1. Combine reactants in a large, tared test tube (provided)
   - use 0.5g of material obtained in step 1
   - remember to keep a small tlc sample
   - CAUTION: KOH is corrosive - avoid spills; handle with care
   - add a glass rod (serves as a boiling stick here)

2. Warm to 160°C and heat for 5 minutes
   - measure temperature inside test tube, not temp of sand bath
   - begin timing when temp inside test tube is 160°C
   - do not let reaction temperature exceed 180°C
   - do not use thermometer to stir; do not leave it in the reaction mixture
   - solid KBr will separate as the reaction proceeds

3. Evaluate reaction progress by TLC
   - spot both the starting material (saved from step 1) & reaction mixture
   - reaction complete - move on to step 4
   - reaction incomplete - heat 5 min more; check by TLC again
   - Q How do you know if the reaction is done??
     - look for the disappearance of starting material (dibromodiphenylethane)
     - look for the appearance of a new spot (product)
     - consider that you also have other reagents in the test tube

4. Cool reaction mixture to room temp; slowly add cold water
   - add cold water dropwise while stirring solution with the glass rod
   - KBr (by-product) is water soluble
   - solid diphenylacetylene will separate

5. Collect product by vacuum filtration
   - rinse product with a small amount of ice cold water
   - dry as best you can
   - save a small sample for melting point

6. Recrystallize product from hot ethanol
   - think about the technique before you arrive!
   - use a minimum amount of hot solvent
   - cool slowly to room temperature; then in ice
   - collect crystals by vacuum filtration
   - dry thoroughly

7. Analyze product(s)
   - TLC (trans-stilbene & all products - crude & recrystallized)
   - melting point of both crude & recrystallized diphenylacetylene

Writing the Lab Report: Exp #6 Dehydration & GC

**Purpose**
- combination synthesis/technique experiment:
  - what will you make? & what will you learn?
  - include a balanced chemical equation for the reaction you ran
    - remember: 1 mole of alcohol gives 1 mole of alkenes (product mix)

**Results & Discussion**
- Don't discuss the procedure in detail
- Comment on the success of your reaction (Did it work?)
  - Bromine test
    - what do you expect to see if your reaction was a success?
    - discuss all results; include known negative/positive
    - make a Table
    - what do your results tell you? Did the reaction work or not?
      - explain! show the reaction your product will undergo
      - will the starting material also react this way?
  - TLC
    - what do you expect to see if the reaction was a success?
      - how should R, values of SM & product differ?
      - explain ➔ relate to compound structure (functionality)
    - do your results indicate that the reaction worked?

Boiling Point
- Is this a good indicator of reaction success? Explain.
**Writing the Lab Report: Exp #6 Dehydration & GC**

**Results & Discussion**
- Comment on the success of your reaction (Did it work?)
  - IR
    - discuss how your IR data support the structure of both the starting alcohol & the product alkenes
    - tabulate IR data as before (one for each compound)
- Comment on the product purity
  - Was the product pure?
  - TLC
    - how can TLC be used to evaluate purity?
  - IR
    - how can you use IR as an indicator of purity?
- Comment on the reaction efficiency
  - Report and comment on your percent yield.

**Conclusion**
- a brief recap of your findings
- was your reaction successful (did you make it? was it pure?)
- include a general statement about gas chromatography (what did you learn? how can the technique be used?)
- do not include a lot of theory

**Calculating Percent Yield**

1. Write a balanced chemical equation
   - use to determine molar ratio of starting material(s) to product(s)
2. Identify the limiting reagent
   - need to know amount of materials used
   - need molecular weights of starting materials & products
   - a catalyst is never the limiting reagent
3. Determine the theoretical yield
   - the maximum amount of product you could possibly recover
4. Calculate % yield
   - \[
     \% \text{ yield} = \frac{\text{amount of product obtained (g)}}{\text{theoretical yield (g)}} \times 100
   \]
Calculating Percent Yield: Example

1. Write a balanced chemical equation

\[ \text{Cl}_2 + \text{NaI} \rightarrow \text{Cl}_2 + \text{NaI} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>amount</th>
<th>MW</th>
<th>1-mole Cl</th>
<th>1-mole NaI</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl_2</td>
<td>0.53g</td>
<td>92.57 g/mol</td>
<td>5.72 mole</td>
<td>1 mole RI</td>
<td>184.02 g/mol</td>
</tr>
<tr>
<td>NaI</td>
<td>2.1g</td>
<td>149.89 g/mol</td>
<td>14.0 mole</td>
<td>2.4 mole</td>
<td>58.44 g/mol</td>
</tr>
</tbody>
</table>

2. Identify the limiting reagent

- calculate moles of reactants
- determine equivalents of reactants

\[ \frac{0.53g \text{ RCl}}{92.57g \text{ RCl}} \times \frac{1 \text{ mole RCl}}{184.02 g \text{ RI}} = 0.0057 \text{ mole RCl} \]

\[ \frac{2.1g \text{ NaI}}{92.57g \text{ NaI}} \times \frac{1 \text{ mole NaI}}{1 \text{ mole NaI}} = 0.0225 \text{ mole NaI} \]

- identify limiting reagent (a catalyst will never be the limiting reagent)

3. Determine the theoretical yield

\[ \text{Cl}_2 \rightarrow \text{Cl}_2 \times \frac{1 \text{ mole RCl}}{1 \text{ mole RCl}} \times \frac{184.02 g \text{ RCl}}{1 \text{ mole RCl}} = 1.05g \text{ RCl} \]

4. Calculate % yield

\[ \% \text{ yield} = \frac{\text{amount of product obtained (g)}}{\text{theoretical yield (g)}} \times 100 \]

\[ = \frac{0.72g \text{ obtained}}{1.05g \text{ theory}} \times 100 = 69\% \]

Lab Practical (October 31 - November 4)

- Format: You will be asked to accomplish specific laboratory tasks within a given time frame; all tasks will involve techniques you have done before e.g. melting point, TLC, recrystallization, extraction, distillation, column chromatography.

- The Lab Practical will be held during your regularly scheduled lab period; there is no make-up for the Lab Practical. Be sure you are there!

- Show up on time! If you are late, you will not get additional time.

- The Lab Practical is closed book; no outside materials of any kind are allowed.

- No calculators or cell phones are allowed.

- Just you, a pencil, and organic chemistry! Come prepared.
**Lab Practical**  (October 31 - November 4)

- **Preparation:** Review procedures & techniques from earlier labs (exp 1-5)
  - topics may include: melting point
  - TLC
  - recrystallization
  - extraction
  - distillation
  - column chromatography
  - Be sure you understand the concepts behind these techniques; You may have to use this knowledge to make decisions about what to do

- **The Good News**
  - no prelab write up is required
  - there is no lab report required for the practical
  - Experiment 7 lab report (alkyne synthesis) is not due until the following week: November 7 - 11
  
  As always, it will be due at the beginning of your regular lab session