Bromination of Alkenes II: Stilbene

Greener Bromination of Stilbene

(Doxee & Hutchison; Green Organic Chemistry; Adapted from John Thompson, Lane Community College)

Purpose: To brominate trans-stilbene using green principles for the purpose of verifying the mechanism.

Techniques & Principles: Reflux, vacuum filtration, melting point determination

Green Principles: Atom Economy, Safer reagents

Safety Concerns: Toxicity of bromine and hydrogen peroxide.

Introduction

In this experiment you will be reacting trans-stilbene with Br₂ forming the addition product across the ethane double bond.

\[
\text{(E)-stilbene} \quad \xrightarrow{\text{Br}_2} \quad \text{1,2-dibromo-1,2-diphenylethane}
\]

trans-Stilbene is an interesting molecule for this reaction because it and its products can be evaluated for stereochemistry simply by melting point determination.

- cis-Stilbene is highly sterically hindered and is therefore not nearly as stable as trans-stilbene.
- cis-Stilbene has a melting point of 5-6°C and trans-stilbene has a melting point of 124-125°C.

Reacting either of these compounds (cis or trans) with Br₂ should produce 1,2-dibromo-1,2-diphenylethane. This product has four possible structures.

- Two of them are actually the same (meso structures) and
- the other two contain two chiral centers, which are optically active and mirror images of each other.

The meso structure has a melting point of 238-243°C and a racemic mixture of the other products have a melting point of 113-114°C.

Reading Notes

- **Vicinal dibromide** – (Latin, *vicinus* meaning neighboring) two bromine atoms bonded to C atoms adjacent to each other. This is in comparison to:
- **Geminal dibromide** – (Latin, *geminus* meaning twin) two bromine atoms bonded to the same C atom.
- Br₂ is formed *in situ* by the reaction of HBr and H₂O₂.

Link to Procedures: [http://greenchem.uoregon.edu/Pages/Overview.php?ID=81](http://greenchem.uoregon.edu/Pages/Overview.php?ID=81)
**Post Lab Questions:**
1. Draw out the accepted mechanism for reaction of bromine with tran-stilbene.
2. Discuss how your experiment gives evidence for or against the accepted bromine reaction mechanism. Be clear and detailed in your discussion.
3. Evaluate this experiment in terms of its greenness.
   - Compare HBr/H$_2$O$_2$ to using elemental Br$_2$ as in the bromination of tomatoes.
   - Overall greenness of this reaction
   - What recommendations do you have to improve the green character of this reaction?
1. Considering the chemicals used for this experiment. What safety procedures are necessary beyond wearing goggles and gloves?

2. Our supply of trans-stilbene is not new. Would you expect it to be contaminated by cis-stilbene? Explain.

3. Draw the following structures and give their melting or boiling points.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>mp or bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>trans-stilbene</td>
<td>mp</td>
</tr>
<tr>
<td>B.</td>
<td>(1R,2S)-1,2-dibromo-1,2-diphenylethane</td>
<td>mp</td>
</tr>
<tr>
<td>C.</td>
<td>(1S,2R)-1,2-dibromo-1,2-diphenylethane</td>
<td>mp</td>
</tr>
<tr>
<td>D.</td>
<td>(1S,2S)-1,2-dibromo-1,2-diphenylethane</td>
<td>mp</td>
</tr>
<tr>
<td>E.</td>
<td>(1R,2R)-1,2-dibromo-1,2-diphenylethane</td>
<td>mp</td>
</tr>
</tbody>
</table>

   - Which of the above stereoisomers of dibromodiphenyl ethane would be meso? _____
   - Which of the above stereoisomers of dibromodiphenyl ethane would make up a racemic mixture? _____
   - Which of the possible stereoisomers would arise from the anti-addition of bromine to trans-stilbene? _____
   - Which of the possible stereoisomers would arise from the syn-addition of bromine to trans-stilbene? _____

4. This week’s laboratory experiment allows us to evaluate whether the proposed anti mechanism for bromination of alkenes is possible or not. How could this experiment prove or disprove the proposed mechanism? (Be specific about how will you know.)
5. Draw the set up needed for reflux. Show position of clamps.

6. Recreate the following table of chemical data in your notebook:

<table>
<thead>
<tr>
<th><strong>Compound</strong></th>
<th>M.M. (g/mol)</th>
<th>Gs or mLs used/obtained</th>
<th>Moles used/obtained And % yield</th>
<th>mp or bp (°C)</th>
<th>Safety or hazard concerns associated with this chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td></td>
<td></td>
<td></td>
<td>b.p</td>
<td></td>
</tr>
<tr>
<td><em>trans</em>-stilbene</td>
<td></td>
<td></td>
<td></td>
<td>m.p</td>
<td></td>
</tr>
<tr>
<td>Hydrobromic acid: (HBr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen peroxide (30% H₂O₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meso-1,2-dibromo-1,2-diphenylethane</td>
<td></td>
<td></td>
<td></td>
<td>m.p</td>
<td></td>
</tr>
<tr>
<td>Racemic-1,2-dibromo-1,2-diphenylethane</td>
<td></td>
<td></td>
<td></td>
<td>m.p</td>
<td></td>
</tr>
</tbody>
</table>