Experiment 9

Phase Transfer Catalyst: Addition of Dichlorocarbene to Cyclohexene

Objectives
- To understand the role of a phase-transfer agent in a heterogeneous reaction
- To produce a reactive carbene intermediate that reacts with the double bond in cyclohexene to produce substituted dichlorocyclopropane.

In the Lab
- Students work in pairs

After Lab
- Complete the Chem21 assignment

Waste
- Rinse the RBF used at the rotary evaporator with acetone and place the rinse solution in the waste container labeled Acetone Waste located in the Instructor’s hood.

Safety
- Students must wear goggles for this experiment.
- Wear gloves when dispensing the 50% KOH.
The reaction above will not occur without the help of a phase-transfer catalyst – a tetra-alkyl ammonium ion in this particular case. The reason is simple. The hydroxide ion is not soluble in organic liquids (i.e. chloroform) and chloroform (CHCl₃) is immiscible in water. **How do we get the OH⁻ and the CHCl₃ to react??** We will employ a **phase-transfer agent**. These polar organic compounds are soluble to some extent in both the aqueous and the organic layers. They are soluble in the organic layer because they possess many carbons and they are soluble in the aqueous layer because one of its atoms (the nitrogen) carries a positive charge. While in the aqueous layer, this positive ammonium ion “picks up” a hydroxide anion and transports it to the organic layer. Once there, a reaction ensues between the hydroxide and chloroform producing dichlorocarbene (CCl₂). This reactive intermediate, produced in the organic layer where cyclohexene is located, reacts immediately with cyclohexene’s double bond and produces a dichlorocyclopropane.

In addition, many other anions can be transported by phase transfer agents leading to reactions that otherwise would not have occurred. Also, it is important to note that the transported anions are better nucleophiles in the organic phase than in the aqueous phase since they are not solvated by water molecules (i.e. there are very few intermolecular attractive forces present in the organic layer to help stabilize the negative charge on the anions).
### Table of Physical Constants

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Formula</th>
<th>Molecular Weight</th>
<th>Boiling Point</th>
<th>Density</th>
<th>$n_D^{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>C$<em>6$H$</em>{10}$</td>
<td>82.15</td>
<td>83</td>
<td>0.811</td>
<td>1.4460</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl$_3$</td>
<td>119.38</td>
<td>61</td>
<td>1.492</td>
<td>1.4460</td>
</tr>
<tr>
<td>Potassium Hydroxide</td>
<td>KOH</td>
<td>56.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzyltributyl ammonium chloride</td>
<td>C$_7$H$_7$(C$_4$H$_9$)$_3$N$^+$Cl$^-$</td>
<td>311.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>NaCl</td>
<td>58.44</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Magnesium Sulfate</td>
<td>MgSO$_4$</td>
<td>120.37</td>
<td></td>
<td>2.660</td>
<td></td>
</tr>
<tr>
<td>7,7-Dichloronorcarane</td>
<td>C$<em>7$H$</em>{10}$Cl$_2$</td>
<td>165.06</td>
<td>193</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1
Experiment 9 • 7,7-Dichloronorcarane

Procedure:
1. Place 18 ± 2 mL 50% KOH in a 500 mL Erlenmeyer flask equipped with a 1½ - 2 inch Teflon stir bar.
2. Place all of the cyclohexene you produced in Lab 8 [Data Sheet] and 25 ± 3 mL of chloroform into the same Erlenmeyer flask.
3. Add 1.0 ± .1 g of the phase-transfer catalyst benzyltriethylammonium chloride (Avoid contact with skin and reclose the bottle immediately) to the Erlenmeyer flask.
4. Place a 50 mL Erlenmeyer flask upside down in the neck of the flask. Clamp the 500 mL Erlenmeyer flask and stir as vigorously as possible (set stirrer to ~8).
5. Let it stir vigorously for 1 hour. It should heat up slightly and become frothy as the reaction proceeds.
   - Work on Lab 8 Post-lab problems during this hour.
6. After 1 hour, turn the stir off and transfer the mixture to a 250 mL separatory funnel.

Separatory Funnel:
   - Set the separatory funnel in a ring on a ring stand.
   - Make sure the stopcock is closed before pouring in the solution!
   - Put a stopper that doesn’t leak in the top.
   - When draining, the stopper must be out, or it will not drain.
   - Always keep all layers in labeled beakers until the end of lab!

7. Add 75 ± 5 mL of water to the 500-mL Erlenmeyer flask, swirl and add this to the separatory funnel.
8. Add 20 ± 3 mL of chloroform to the 500 mL Erlenmeyer flask, swirl to dissolve any remaining product (the solid is not your product), and place this solution in the separatory funnel.
9. Shake the funnel vigorously (vent as needed), allow the layers to separate and drain the lower chloroform layer into a clean, dry beaker.
10. Re-extract the aqueous layer that remains in the separatory funnel with another 20 ± 3 mL portion of chloroform. Drain this lower organic layer into the same container as the first chloroform layer.
11. **Place the aqueous layer in a labeled beaker** and, at the end of lab, discard it in the Aqueous Waste Beaker located in the hood (avoid contact with the skin).
12. Rinse the separatory funnel with water to remove any material remaining from the first extraction.
13. Pour the combined organic layers (the CHCl₃ layers) from Steps 9 and 10 into the separatory funnel.
14. Wash the organic layer with 30 ± 3 mL of a saturated sodium chloride solution and allow the layers to separate.
15. Place ~2 ± .2 g of anhydrous magnesium sulfate into an Erlenmeyer flask and drain the lower chloroform layer into this flask.
16. Swirl the mixture occasionally for 10 minutes to completely dry the organic layer.
17. Place a fluted filter paper in a glass funnel whose stem extends into a pre-weighed 250 mL RBF [Data Sheet]. Gravity filter the dry solution of 7,7-dichloronorcarane and CHCl₃.
18. Remove the solvent (chloroform) via rotary evaporation.
19. Weigh the 250 mL RBF [Data Sheet] after removing the chloroform via rotary evaporation.
20. Determine the mass of 7,7-dichloronorcarane [Online Calculation].
21. Transfer the 7,7-dichloronorcarane to a glass vial and affix the label below.

**Lab Report**

Once you have turned in your Instructor Data Sheet, lab attendance will be entered and you will have access to enter your lab data online and begin the lab submission process. Enter you lab data before exiting the lab - **enter your data accurately to avoid penalty**. The lab program will take you in order to each calculation. Mouse over the orange “TOL” link to see the points and tolerances for each calculation.

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**Lab 9**

**Synthesis of 7,7-Dichloronorcarane**

**Name:**

**Mass:** g
Synthesis of 7,7-Dichloronorcarane

Student Data Sheet

Mass of Cyclohexene used

Mass of the 250 mL round bottom flask

Mass of 7,7-dichloronorcarane and the 250 mL flask

Name: _______________________
Partner: _____________________

Synthesis of 7,7-Dichloronorcarane

Instructor Data Sheet

Mass of Cyclohexene used

Mass of the 250 mL round bottom flask

Mass of 7,7-dichloronorcarane and the 250 mL flask