CHAPTER 9

Chirality does not necessary require stereogenic centers. Helical chirality can exist in special cases where the molecules are restricted by rotation. For example, the allene shown below does not contain a stereogenic center, but it is chiral. When viewed down the axis of the carbons of the allene, following the substituents from front to back is opposite for the two mirror images.

![Allene structure with substituents]

CHAPTER 10

Alkyl halides are found in many common solvents and materials.

- CH₂Cl₂
- CH₂CICH₂Cl
- CHCl₃
- F₃C-CHBrCl (Halothane, an anesthetic)

The carbon-halide bond strength gets weaker as you move from fluorine to iodine. This correlates to the change in bond length. Alkyl halides are good electrophiles!

<table>
<thead>
<tr>
<th>Halide</th>
<th>C-X length</th>
<th>C-X bond strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluoromethane</td>
<td>CH₃F 1.39 Å</td>
<td>108 kcal/mol</td>
</tr>
<tr>
<td>chloromethane</td>
<td>CH₃Cl 1.78 Å</td>
<td>84 kcal/mol</td>
</tr>
<tr>
<td>bromomethane</td>
<td>CH₃Br 1.93 Å</td>
<td>70 kcal/mol</td>
</tr>
<tr>
<td>iodomethane</td>
<td>CH₃I 2.14 Å</td>
<td>56 kcal/mol</td>
</tr>
</tbody>
</table>

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Remember how we have prepared alkanes from double bonds -- Addition of H-X and X₂.

Free radical halogenation of alkanes will produce alkyl halides, but usually mixtures of products result. Radical halogenation does not give simple statistical mixtures.

For the Chlorination of butane, a 30 : 70 mixture of secondary and primary products are produced. Statistics would predict 40 : 60 from the substitution of 4 possible secondary hydrogens and 6 possible tertiary hydrogens. Thus, secondary H's are 3.5 times more reactive than primary H's.

\[
\text{Cl}_2 \text{light} \quad \begin{array}{c}
\text{expected ratio from 6 1° H's and 4 2° H's} \\
6 : 4
\end{array}
\]

\[
\text{Actual Ratio Found} \quad 30 : 70
\]

2° H's are 3.5 times more reactive than 1° H's toward radical chlorination

Chlorination of 2-methylpropane shows the difference in the reactivity of tertiary H's vs. primary H's. Statistically, a 90 : 10 mixture should be obtained from substitution of one of 9 possible primary H's and 1 possible tertiary H. Tertiary H's are 5 times more reactive than primary H's.

\[
\text{Cl}_2 \text{light} \quad \begin{array}{c}
\text{expected ratio from 9 1° H's and 1 3° H's} \\
1 : 9
\end{array}
\]

\[
\text{Actual Ratio Found} \quad 35 : 65
\]

3° H's are 5 times more reactive than 1° H's toward radical chlorination