## Summary of Alkene Reactions

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reagent</th>
<th>What adds?</th>
<th>To give the more stable:</th>
<th>Which upon reaction with:</th>
<th>Yields</th>
</tr>
</thead>
</table>

### Hydrohalogenation:

- \[
  \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{HBr} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2\text{Br} + \text{H}_2\text{O} + \text{H}^+ \]
- **Yields:** 

### Radical Hydrohalogenation:

- \[
  \text{CH}_3\text{CH} = \text{CH}_2 + \text{HBr}/\text{peroxides} + \text{Br}^- \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{Br} + \text{H}_2\text{O} + \text{Br}^- \]
- **Yields:** 

### Hydration:

- \[
  \text{CH}_3\text{CH} = \text{CH}_2 + \text{H}_2\text{SO}_4 + \text{H}^+ \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{OH} + \text{H}_2\text{O} + \text{H}^+ \]
- **Yields:** 

### Halogenation:

- \[
  \text{CH}_3\text{CH} = \text{CH}_2 + \text{X}_2 \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{X} + \text{H}_2\text{O} + \text{X}^- \]
- **Yields:** 

### Halohydrin Formation:

- \[
  \text{CH}_3\text{CH} = \text{CH}_2 + \text{X}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{X} + \text{H}_2\text{O} + \text{X}^- \]
- **Yields:** 

### Hydroboration/Oxidation:

- \[
  \text{CH}_3\text{CH} = \text{CH}_2 + \text{B}_2\text{H}_6 + \text{H}^-\text{BH}_2 \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{BH}_2 + \text{HO}_2\text{NaOH} + \text{H}_2\text{O} \]
- **Yields:** 

### Oxymercuration:

- \[
  \text{CH}_3\text{CH} = \text{CH}_2 + \text{Hg}^+\text{(Ac)} + \text{ROH} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{Hg}^+\text{(Ac)} + \text{H}_2\text{O} \]
- **Yields:** 

### Notes:

- **\( \beta \)-Mercury-substituted carbocation:** replaces \( \text{Hg}^+\text{(Ac)} \) with \( \text{H}^-\)
Bicyclic compounds require the breaking of two carbon-carbon bonds to convert them to open
cained compounds--containing no rings.

Bicyclic compounds are named by prefixing bicyclo- to the name of the parent hydrocarbon.
The name of the parent hydrocarbon is obtained by counting the total number of carbon atoms
in all of the rings of the compound. Thus, because norbornane (below) contains seven carbon
atoms in the two rings of the molecule it is a bicycloheptane. Carbon atoms shared by both
rings are referred to as bridgehead carbons.

The numbers of carbon atoms between bridgehead carbons in the molecule are
specified by counting from the bridgehead carbon and listing each of the numbers in brackets
in decreasing order prior to the name of the hydrocarbon. Thus, norbornane is
bicyclo[2.2.1]heptane. The following are additional examples of bicycloheptanes:
The carbon positions of a bicyclic hydrocarbon are numbered from the bridgehead carbon around the largest ring first. Substituents are located by the number assigned to the carbon positions. For example:

\[
\text{1,7,7-trimethylbicyclo[2.2.1]heptane}
\]

\[
\text{1,3-dimethylbicyclo[1.1.0]butane}
\]

\[
\text{bicyclo[2.2.2]octa-2,5,7-triene}
\]
The Curved Arrow Formalism

Curved arrows are used by chemists to indicate the flow of electrons in reactions.¹

1. For each electron pair (either a bonding pair or lone pair) that changes position in a reaction, **one arrow** is required.
   - The tail of the arrow starts at the initial position of the electron pair (at an atom for a lone pair; at a bond for a bonding pair).
2. The head of the arrow points to the new position of the electron pair (to an atom for formation of a lone pair; midway between atoms for formation of a bond.)
3. CURVED ARROWS DO NOT REPRESENT THE MOVEMENT OF NUCLE!!!

4.

Ex. 1

Ex. 2

Ex. 3

Note strict balance of charge and that only red electrons are moving (all other electrons and atomic positions remain the same). Keep careful track of formal charges.

¹They are also sometimes used to indicate the interconversion of resonance forms. Do not confuse the two usages — interconversion of resonance forms is not a reaction!!
# Guide to Displacement Reactions

## Reactivity

<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>$S_N1$ (carbocation intermediate)</th>
<th>$E1$ (carbocation intermediate)</th>
<th>$S_N2$ (concerted)</th>
<th>$E2$ (concerted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°</td>
<td>![X]</td>
<td>![X]</td>
<td>• good LG</td>
<td>• strong, bulky bases</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• good Nu:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• polar aprotic solvent</td>
<td></td>
</tr>
<tr>
<td>2°</td>
<td>• good LG</td>
<td>• competes with $S_N1$ when base is present</td>
<td>• good LG</td>
<td>• competes with $S_N2$</td>
</tr>
<tr>
<td></td>
<td>• poor Nu:</td>
<td></td>
<td>• good Nu:</td>
<td>• favored by bulky bases stronger than HO$^-$</td>
</tr>
<tr>
<td></td>
<td>• polar protic solvent</td>
<td></td>
<td>(weaker base than HO$^-$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• polar aprotic solvent</td>
<td></td>
</tr>
<tr>
<td>3°</td>
<td>• good LG</td>
<td>• competes with $S_N1$ when base is present</td>
<td>![X]</td>
<td>• strong base</td>
</tr>
<tr>
<td></td>
<td>• any Nu:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• polar protic solvent</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Nucleophilicity

<table>
<thead>
<tr>
<th>Classification</th>
<th>Nucleophiles</th>
<th>Rel. React.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>I$^-$, HS$^-$, RS$^-$</td>
<td>$&gt;10^5$</td>
</tr>
<tr>
<td>Good</td>
<td>Br$^-$, HO$^-$, RO$^-$, CN$^-$, N$_3^-$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Fair</td>
<td>NH$_3$, Cl$^-$, F$^-$, RCO$_2^-$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Weak</td>
<td>H$_2$O, ROH</td>
<td>1</td>
</tr>
<tr>
<td>Very Weak</td>
<td>RCO$_2$H</td>
<td>$10^{-2}$</td>
</tr>
</tbody>
</table>

## Leaving Groups

<table>
<thead>
<tr>
<th>Classification</th>
<th>Leaving Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>ROSO$_2^-$, H$_2$O, ROH, N$_2$</td>
</tr>
<tr>
<td>Good</td>
<td>I$^-$, Br$^-$, Cl$^-$, NR$_3$, RCO$_2^-$</td>
</tr>
<tr>
<td>Poor</td>
<td>HO$^-$, RO$^-$, F$^-$, CN$^-$, NH$_2$</td>
</tr>
<tr>
<td>Substrate</td>
<td>H$_2$SO$_4$ (dil.)</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------</td>
</tr>
<tr>
<td></td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td><img src="image5" alt="Image" /></td>
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<tr>
<td></td>
<td><img src="image9" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td><img src="image13" alt="Image" /></td>
</tr>
</tbody>
</table>

*Give all possible products, including stereochemistry!*
| Substrate | Reagent | \( \text{Cl}_2 \) \( \text{H}_2\text{O} \) | 1. \( \text{Hg(OAc)}_2 \) 
2. \( \text{NaBH}_4/\text{OH}^- \) | 1. \( \text{BH}_3 \) 
2. \( \text{H}_2\text{O}_2/\text{OH}^- \) | 1. \( \text{OsO}_4 \) 
2. \( \text{H}_2\text{O}_2/\text{OH}^- \) |
| --- | --- | --- | --- | --- | --- |

Give all possible products, including stereochemistry!
Analysis of Isomerism

Two molecules with the same molecular formula

Superimposable?

YES → Molecules are Identical

NO → Molecules are Constitutional Isomers

Same Connectivity?

YES → Mirror Images?

NO → Molecules are Diastereomers

YES → Molecules are Enantiomers
Note: It should become second nature to recognize the common Lewis configurations for C, N, and O

\[
\begin{align*}
\text{C}^- \quad \text{,} \quad \equiv \text{C} \quad \equiv \text{C}^- & \quad 0 \text{ Formal Charge} \\
\text{C}^+ & \quad +1 \text{ Formal Charge} \\
\text{C}^- & \quad -1 \text{ Formal Charge} \\
\text{C} & \quad \text{NO!!! Violates Octet Rule}
\end{align*}
\]

\[
\begin{align*}
\equiv \text{O} & \quad \equiv \text{O}^{-} \quad 0 \text{ Formal Charge} \\
\text{O} & \quad -1 \text{ Formal Charge} \\
\text{O}^+ & \quad +1 \text{ Formal Charge}
\end{align*}
\]

\[
\begin{align*}
\equiv \equiv \equiv & \quad 0 \text{ Formal Charge} \\
\equiv \equiv & \quad +1 \text{ Formal Charge} \\
\equiv \equiv & \quad -1 \text{ Formal Charge}
\end{align*}
\]
LEWIS STRUCTURES OFTEN DO NOT ADEQUATELY REPRESENT ACTUAL STRUCTURES:

Implies unequal bonding of N to two oxygens!
Experimentally, they are the same length!

Linus Pauling (Feb. 28, 1891-Aug. 19, 1994) introduced the concept of...

**RESONANCE THEORY**

Resonance: When a molecule can be represented by 2 or more Lewis structures where the arrangement of atoms is the same, but electrons are shifted

The small curved arrows are "electron pairing" arrows. They represent the figurative movement of an electron pair.
This is for bookkeeping purposes only!

Resonance arrow (double headed): Do not indicate any resonance or equilibrium arrows!

Remember...

A. Neither Lewis structure by itself represents reality. The structures are not rapidly interconverting. Rather, the actual structure is a mix of the two (or more) resonance forms and is called a...

- RESONANCE HYBRID (kind of like blue and yellow mixing to make green)

B. THE ACTUAL MOLECULE IS MORE STABLE THAN ANY INDIVIDUAL RESONANCE FORM IMPLIES. IN FACT, THE MORE RESONANCE FORMS ONE CAN DRAW OF A SPECIES, THE MORE STABLE IT IS.

C. OZONE, O₃, APPEARS TO HAVE A SEPARATION OF CHARGE, IMPLYING SEVERE INSTABILITY...

- THE RESONANCE HYBRID SHOWS THAT BOTH TERMINAL OXYGENS SHARE THE NEGATIVE CHARGE, RESULTING IN GREATER STABILITY

**RULES OF RESONANCE THEORY**

1. ATOMIC POSITIONS REMAIN THE SAME

- are not resonance forms!!

- are resonance forms!!

2. FOLLOW THE OCTET RULE

are valid resonance forms, but...

...is not!

3. RESONANCE FORMS FOR A GIVEN MOLECULE NEED NOT CONTRIBUTE EQUALLY TO THE OVERALL STRUCTURE (THE RESONANCE HYBRID) SINCE THEY MAY DIFFER IN ENERGY

- Separation of charge indicates a higher energy resonance form...

- more stable contributes more

- less stable contributes less

- Formal negative charge on electropositive elements indicates a higher energy resonance form, as well as positive charge on electronegative elements...

- more stable (O⁻ on O) less stable (O⁻ on O)

4. INSURE THAT ALL RESONANCE FORMS HAVE THE SAME NET CHARGE, THE SAME NUMBER OF ELECTRONS, AND THE SAME NUMBER OF UNPAIRED ELECTRONS

-
**Orbital Hybridization**

**Linear Carbon (Atom)**
- Only two other atoms or
- One atom and one lone pair surrounding carbon atom

\[(\text{one } s + \text{ one } p) \rightarrow \text{two } sp \text{ orbitals}\]

**Trigonal Planar Carbon (Atom)**
- Only three other atoms or
- Two atoms and one lone pair or
- One atom and two lone pairs (rare)

\[(\text{one } s + \text{ two } p) \rightarrow \text{three } sp^2 \text{ orbitals}\]

**Tetrahedral Carbon (Atom)**
- Four other atoms or
- Three atoms and one lone pair or
- Two atoms and one lone pair

\[(\text{one } s + \text{ three } p) \rightarrow \text{four } sp^3 \text{ orbitals}\]

**Orient Them:**
- 180° apart
- 120° apart
- 109.5° apart

\[2p \text{ hybrid orbitals}\]

\[\text{Two } p \text{ orbitals left over}\]

\[\sigma \text{ bonds are formed by the } sp \text{ hybrids and } \pi \text{ bonds by the } p \text{ orbitals}\]

**Example**
- Hydrogen cyanide
  \[\text{H} = \text{C} = \text{N} :\]
  \[(\text{side view})\]
  \[(\text{top view})\]

**Example**
- Ethylene
  \[\text{H} = \text{C} \equiv \text{C} = \text{H}\]

**Example**
- Methane
  \[\text{H} = \text{C} - \text{H}\]