Organic Reactions Summary
Alkenes, alkynes and variations

For Use as a Study Guide

Beauchamp
Making alkenes and alkynes

a. mechanism using potassium t-butoxide, KOC(CH₃)₃, S_N2 at and E2 at 1°, 2° and 3° RBr,

Example reactions

- [Structure diagram] Br → KOC(CH₃)₃ → E2 > S_N2 anti elimination
- [Structure diagram] Br → R → KOC(CH₃)₃ → E2
- [Structure diagram] Br → KOC(CH₃)₃ → E2
- [Structure diagram] S → KOC(CH₃)₃ → E2
- [Structure diagram] Br → KOC(CH₃)₃ → S_N2 no other option
b. Double elimination from dibromoalkanes to form alkynes and terminal acetylides used in many additional reactions ($\text{S}_2\text{N}_2$ with RBr, C=O addition to aldehydes and ketones, and reaction with epoxides)

The zipper reaction moves a triple bond in an unbranched linear chain to the end and allows all of the above reactions.
c. mechanism using NaCC-R to make a bigger alkyne, $S_N2$ at methyl, $1^\circ$ and $2^\circ$ RBr and only E2 at $3^\circ$ RBr,

\[ \text{Example reactions} \]

<table>
<thead>
<tr>
<th>Reaction Details</th>
<th>Structure 1</th>
<th>Structure 2</th>
<th>Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_N2$ inversion of configuration</td>
<td>$\text{SN2}$</td>
<td>$\text{SN2}$</td>
<td>$\text{SN2}$</td>
</tr>
<tr>
<td>$E2 &gt; S_N2$</td>
<td>$\text{E2}$</td>
<td>$\text{E2}$</td>
<td>$\text{E2}$</td>
</tr>
<tr>
<td>Achiral</td>
<td>$\text{achiral}$</td>
<td>$\text{achiral}$</td>
<td>$\text{achiral}$</td>
</tr>
</tbody>
</table>
d. mechanism using triphenylphosphine to make triphenyolphosphonium salt, $S_N2$ at methyl, $1^o$ and $2^o$ RBr and only E2 at $3^o$ RBr, used to make a triphenyolphosphonium ylid to make Z and E alkenes with aldehydes and ketones.

\[ \text{Ph} = \text{phenyl} \]

Schlosser Modification of the Wittig reaction to make E alkenes

\[ \text{Ph}_3\text{P} = \text{O} \]

\[ \text{betaine} \]

The stereochemistry of the alkene is determined in this step.
Example reactions

1. Br
2. n-BuLi
3. CH$_3$CH=O

Normal Wittig
Z alkene preferred

1. Br
2. n-BuLi
3. CH$_3$CH=O

Normal Wittig
Z alkene preferred

1. Br
2. n-BuLi
3. CH$_3$CH=O

E2

1. Br
2. n-BuLi
3. CH$_3$CH=O

Normal Wittig
Z alkene preferred

1. Br
2. n-BuLi
3. CH$_3$CH=O

Normal Wittig
Z alkene preferred

1. Br
2. n-BuLi
3. CH$_3$CH=O

Schlosser modification
of the Wittig
E alkenes preferred

e. Ohira-Bestmann modification of the Seyferth-Gilbert reaction (makes terminal alkynes from aldehydes and a special ‘Wittig’ reagent). Overall reaction from aldehyde to the terminal alkyne – simplified Ohira-Bestmann reaction
Possible mechanism – with mechanism details

Example reactions

difficult to make alkyne at branch point

difficult to make alkyne at branch point

difficult to make alkyne at branch point
f. ROH with sulfuric acid / heat. Synthesis of alkenes (our only useful E1 reaction. Rearrangement is possible).

Example reactions

\[
\begin{align*}
\text{ROH} & \xrightarrow{\text{H}_2\text{SO}_4 / \Delta} \text{alkene} \\
\text{H}_2\text{SO}_4 / \Delta & \xrightarrow{} \text{E2}
\end{align*}
\]

\[
\begin{align*}
\text{ROH} & \xrightarrow{\text{H}_2\text{SO}_4 / \Delta} \text{alkene} \\
\text{H}_2\text{SO}_4 / \Delta & \xrightarrow{} \text{E1}
\end{align*}
\]

\[
\begin{align*}
\text{ROH} & \xrightarrow{\text{H}_2\text{SO}_4 / \Delta} \text{alkene} \\
\text{H}_2\text{SO}_4 / \Delta & \xrightarrow{} \text{E1}
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\begin{align*}
\text{ROH} & \xrightarrow{\text{H}_2\text{SO}_4 / \Delta} \text{alkene} \\
\text{H}_2\text{SO}_4 / \Delta & \xrightarrow{} \text{E1}
\end{align*}
\]
g. Making Allylic Alcohols from Epoxides using LDA (E2 reaction using LDA + epoxides)

Example reactions:

1. LDA, -78°C
2. workup

allylic alcohols, can oxidize to C=O

allylic alcohols, can oxidize to C=O

allylic alcohols, can oxidize to C=O
Reactions of alkenes, alkynes and conjugated variations

a. RBr from alkenes (anti-Markovnikov addition of HBr using free radical chemistry):

mechanism using HBr / ROOR / hv for free radical addition to alkane pi bonds (anti-Markovnikov addition = Br adds to less substituted position to form most stable free radical intermediate, and then H adds to more substituted position)

overall reaction

1. initiation (two steps)

2a propagation

2b propagation

3. termination = combination of two free radicals - relatively rare because free radicals are at low concentrations

Example reactions

\[ \text{H-Br} / \text{hv} \]

\[ \text{Br}_2 / \text{hv} \]
b. RBr from alkenes (anti-Markovnikov addition of HBr using borane chemistry):

mechanism using 1. BH₃  2. Br₂ / CH₃O⁻ for anti-Markovnikov addition of H-Br to alkane pi bonds (concerted, syn addition of H-BH₂ to alkene pi bond, followed by complex with Br₂ and migration of R group to Br)

overall reaction

step 1

syn addition, with H at more substituted position and B at less substituted position.

step 2

Example reactions
c. Alkenes with aqueous sulfuric acid. Alcohol synthesis (Markovnikov addition, rearrangements are possible).

\[
\text{alkene + water} \xrightarrow{\text{acid catalysis}} \text{alcohol}
\]

\[
\text{alkene + alcohol} \xrightarrow{\text{acid catalysis}} \text{ether}
\]

**Example Reactions**

\[
\text{H}_2\text{SO}_4 / \text{H}_2\text{O} \quad (\text{H}_3\text{O}^+)^\bullet
\]

\[
\text{OH} \quad \text{hydration} \quad \text{achiral}
\]

\[
\text{H}_2\text{SO}_4 / \text{H}_2\text{O} \quad (\text{H}_3\text{O}^+)^\bullet
\]

\[
\text{OH} \quad \text{hydration} \quad \text{enantiomers (R and S)}
\]
d. Alkenes with alcohol + sulfuric acid. Markovnikov addition, ether synthesis (rearrangements are possible).
e. Alkenes with 1. \( \text{HgX}_2 / \text{H}_2\text{O} \)  2. \( \text{NaBH}_4 \). Alcohol synthesis with minimal rearrangements (Markovnikov).

The initial adduct is a stable, organomercury compound, but is not usually isolated. It is relatively toxic and need not be isolated. The next step can be run in the same reaction pot (reduction of mercury with \( \text{NaBH}_4 \)).
SN₂ nucleophilic attack by hydride at the mercury atom displaces acetate as the leaving group. Acetate can complex at boron taking the place of the transferred hydride. This keeps boron with an octet, which also is negatively charged.

Free radical dissociation of the weak Hg-C bond occurs. Other free radical reactions are possible here, but not emphasized in our course.

A hydrogen atom is abstracted from the mercury by the highly reactive carbon free radical. This forms mercury metal as one of the products. No stereoselectivity is observed here because of the sp² free radical carbon.

Example Reactions

1. HgX₂ / H₂O
2. NaBH₄

OH
achiral

OH
enantiomers R and S

OH
enantiomers R and S

OH
achiral

OH
achiral

no rearrangement

diastereomers SR and SS
f. Alkenes with 1. $\text{HgX}_2$ / ROH  2. NaBH₄. Ether synthesis with minimal rearrangements (Markovnikov).
Example Reactions

1. \( \text{HgX}_2 / \text{CH}_3\text{OH} \)
2. \( \text{NaBH}_4 \)

achtiral

1. \( \text{HgX}_2 / \text{CH}_3\text{OH} \)
2. \( \text{NaBH}_4 \)
enantiomers
\( \text{R} \) and \( \text{S} \)

1. \( \text{HgX}_2 / \text{CH}_3\text{OH} \)
2. \( \text{NaBH}_4 \)
enantiomers
\( \text{R} \) and \( \text{S} \)

1. \( \text{HgX}_2 / \text{CH}_3\text{OH} \)
2. \( \text{NaBH}_4 \)
achiral

1. \( \text{HgX}_2 / \text{CH}_3\text{OH} \)
2. \( \text{NaBH}_4 \)
achiral

1. \( \text{HgX}_2 / \text{CH}_3\text{OH} \)
2. \( \text{NaBH}_4 \)
no rearrangement

diastereomers
\( \text{SR} \) and \( \text{SS} \)

1. \( \text{HgX}_2 / \text{CH}_3\text{OH} \)
2. \( \text{NaBH}_4 \)
achiral
g. **Electrophilic addition of** HCl, HBr, HI to alkenes = Markovnikov addition, synthesis of RX compounds with possible rearrangements

There are two carbon choices for an electrophile to react with. Which carbon gives up the electrons and becomes a carbocation is based on the most stable carbocation that can form (leading to a regioselective reaction). Such a reaction is generally not stereoselective because the flat carbocation allows attack of the nucleophile to both faces. We expect three possible reactions from the carbocation, add a nucleophile, lose a beta proton or rearrange.

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**Example Reactions**

- **H-Br**
  - only shows regioselectivity
  - Markovnikov addition

- **D-I**
  - only shows stereoselectivity
  - (dl) enantiomers
only shows stereoselectivity

shows regioselectivity but not stereoselectivity

shows possible rearrangements

h. Electrophilic addition of HCl, HBr, HI to alkenes = Markovnikov addition, synthesis of RX compounds, can use 1 equivalent or 2 equivalents

shows regioselectivity
i. Electrophilic addition of HCl, HBr, HI to conjugated diene or triene = Markovnikov addition, synthesis of RX compounds, can use 1 equivalent or 2 equivalents

\[ \text{Br} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{H} \quad \text{Br} \]

\[ \text{H}_3\text{C} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \quad \text{H}_3\text{C} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \]

Resonance

Temp = -80°C  
80%  
20%

(a kinetic choice)

Temp = +40°C  
20%  
80%

(a thermodynamic choice when more energy is available)

3º carbocation is best

\[ \text{Br} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{H} \quad \text{Br} \]

\[ \text{H}_3\text{C} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \quad \text{H}_3\text{C} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \]

Resonance

kinetic product  
larger \( \delta^+ \) in intermediate

thermodynamic product  
more stable alkene

1,2 addition - This looks second because the alkenes are conjugated.

1,4 addition least favorable because it breaks conjugation

1,6 addition - This looks best because the alkenes are more substituted and conjugated.
j. Alkenes with Br$_2$ or Cl$_2$. Synthesis of vicinal dihalide (anti addition).

Bromine is a red orange liquid dissolved in the solvent, the color disappears as it is added.

Chlorine is a green gas, dissolved in the solvent.

1,4-addition is the thermodynamic product because the double bond is more substituted (E or Z is possible).

1,2-addition is the kinetic product because bromine attack is faster at the more positive secondary carbon atom.

chlorine is a green gas, dissolved in the solvent.
Alkenes, Alkynes & Variations

**Br**

**Br**

**Br**

**Br**

k. Alkenes with Br₂/H₂O or Cl₂/H₂O. Synthesis of bromohydrin or chlorohydrin (anti + Markovnikov addition).

**Br₂ / CHCl₃ / 0°C**

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
</table>

| 3% | 21% |
| 5% | 71% |

Br₂ / H₂O (or Cl₂ / H₂O)

OH anti + Markovnikov addition

Br₂ / H₂O (or Cl₂ / H₂O)

OH anti + Markovnikov addition

enantiomers R and S
l. Alkenes with \( \text{Br}_2 / \text{ROH} \) or \( \text{Cl}_2 / \text{ROH} \). Synthesis of bromo or chloro “ethers”.

The mechanism for this reaction is given at the beginning of this document.
Alkenes, Alkynes & Variations

1. BH₃
2. H₂O₂ / HO

1. syn addition
2. oxidation

OH

achiral

1. BH₃
2. H₂O₂ / HO

1. syn addition
2. oxidation

OH

diastereomers
SRR and SSS


A weaker -Br-Br bond is broken and a stronger C-Br bond is formed. Bromide is a good leaving group in the strongly basic solution.

similar reactions,
(two more times)

Lewis
acid/base
reaction

A weaker -Br-Br bond is broken and a stronger C-Br bond is formed. Bromide is a good leaving group in the strongly basic solution.


A weaker -Br-Br bond is broken and a stronger C-Br bond is formed. Bromide is a good leaving group in the strongly basic solution.

The transfer of two electron pairs is concerted. The boron and hydrogen atom add from the same face (syn), so this reaction is stereoselective. The boron adds at the less substituted carbon so this reaction is also regioselective. In subsequent reactions the boron can be converted to another group in exactly the same position, so wherever the boron ends up will indicate the position of the actual group introduced (OH or Br for us).

Second step

There is a strong electron pair donor on each side of the equilibrium equation that can complex with trivalent boron, but only the peroxide anion reacts further. All of these are present.

A weaker -O-O- bond is broken and a stronger C-O bond is formed. Hydroxide, HO⁻ is an acceptable leaving group in the strongly basic solution (compatible with the reaction conditions).
1. HBR₂
2. H₂O₂ / HO⁻ anti-Markovnikov addition

anti-Markovnikov addition

aldehyde

ketone

2 ketones

p. Alkenes with CHCl₃ / RO⁻ or CHBr₃ / RO⁻. Carbene synthesis of dihalocyclopropanes.

chloroform (trichloromethane) pKₐ ≈ 25

alkoxide strong base

singlet carbene

A different type of elimination reaction.

"cis" alkenes form "cis" cyclopropane rings

"trans" alkenes form "trans" cyclopropane rings

concerted reaction (occurs in one step)

stereoselective reaction
q. Alkenes with CH₂I₂ / Zn (Simmons-Smith Rxn). Carbenoid synthesis of cyclopropanes.

**Example Reactions**

1. **CHBr₃ / NaOH**
   - Syn addition
   - Enantiomers R and S

2. **CHCl₃ / NaOH**
   - Syn addition
   - Meso
   - RR and SS

3. **CHCl₃ / KOC(CH₃)₃**
   - Syn addition
   - Meso
   - RS and SR

4. **CH₃Br**
   - Syn addition
   - Achiral

5. **CH₃Cl / NaOH**
   - Syn addition
   - Diastereomers SSR and SRS

---

The first pair of dots represents easily lost 4s electrons on zinc, that reduce a C-I bond.

The second pair of dots represents 3d electrons on zinc that are invoked in the metal complex.

Simmons-Smith reaction

The stabilization by the metal makes the complex more stable, and less reactive. This makes the carbenoid complex more selective for the desired reaction.

**Electron donation**

- "cis" alkenes form "cis" cyclopropane rings
- "trans" alkenes form "trans" cyclopropane rings
Example Reactions (Simmons-Smith reaction)

- CH$_2$I$_2$ / Zn(Cu) syn addition
  - enantiomers R and S
  - enantiomers RR and SS
  - meso RS and SR
  - achiral
  - diastereomers SSR and SRS

r. Alkenes with meta chloroperbenzoic acid (mCPBA). Synthesis of epoxides.

mCPBA (peroxycacid) has two electron poor oxygen atoms in the peroxide bond, and the meta-Cl makes them even more electron poor by its inductive effect.

View this complicated group of arrows as two different groupings in the transition state, one of five atoms and one of three atoms. It might be easier to think about this way.

The alkene is electron rich.

<table>
<thead>
<tr>
<th>Costs (bond energy in kcal/mole)</th>
<th>Changes in energy</th>
<th>Gains (bond energy in kcal/mole)</th>
<th>( \Delta H = -44 \text{ kcal/mole} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O (even trade) = +176</td>
<td></td>
<td>C=O (even trade) = -176</td>
<td>exothermic, even with ring strain</td>
</tr>
<tr>
<td>O-H (even trade) = +110</td>
<td></td>
<td>O-H (even trade) = -110</td>
<td></td>
</tr>
<tr>
<td>O-O (very weak) = +45</td>
<td></td>
<td>C-O (very weak) = -90</td>
<td></td>
</tr>
<tr>
<td>C=C (weak pi bond) = +64</td>
<td>+27</td>
<td>C-O (very weak) = -90</td>
<td></td>
</tr>
<tr>
<td>ring strain of an epoxide is also a cost</td>
<td>Total = +422</td>
<td>Total = -466</td>
<td></td>
</tr>
</tbody>
</table>
Ar
\[
\begin{align*}
\text{O} & \quad \text{enantiomers} \\
\text{H} & \quad \text{R and S} \\
\end{align*}
\]

Ar
\[
\begin{align*}
\text{O} & \quad \text{RR and SS} \\
\text{H} & \quad \text{syn addition} \\
\end{align*}
\]

Ar
\[
\begin{align*}
\text{O} & \quad \text{syn addition} \\
\text{H} & \quad \text{messo} \quad \text{RS and SR} \\
\end{align*}
\]

Ar
\[
\begin{align*}
\text{O} & \quad \text{syn addition} \\
\text{H} & \quad \text{messo} \quad \text{RS and SR} \\
\end{align*}
\]

Ar
\[
\begin{align*}
\text{O} & \quad \text{achiral} \\
\end{align*}
\]

Ar
\[
\begin{align*}
\text{O} & \quad \text{syn addition} \\
\text{H} & \quad \text{diastereomers} \quad \text{SSR and SRS} \\
\end{align*}
\]
s. Alkenes with OsO₄ or KMnO₄. “Syn” synthesis of vicinal diols.

The alkene is electron rich

KMnO₄ and OsO₄ are electron poor

The stereochemistry is set at this point as "syn" addition

Use analogies with hydroxide hydrolysis of esters and imides presented earlier.

OsO₄ has a similar mechanism.

Very expensive OsO₄ can be continually reoxidized with an inexpensive amine oxide (like morpholine N-oxide)

Example Reactions
t. Alkenes with 1. O₃ / -78°C  2. CH₃SCH₃ or Zn. Synthesis of aldehydes or ketones.

Ozone is an electron poor oxidizing reagent.

Simple alkenes are electron rich.

The C=C is completely cleaved at -78°C. The second step decides what will happen to the ozonide. In this example, it is reduced by DMS to two carbonyl compounds, (an aldehyde and a ketone).

**Example Reactions**

1. O₃ / -78°C
2. CH₃SCH₃

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---

---

Example Reactions

Example Reactions

1. $O_3$ / -78°C  2. $H_2O_2$ / HO$^-$

---

[Diagram of the ozonide reaction and peroxide intermediate with rearrangement of peroxide (hydride shift)]

---

Example Reactions

1. $O_3$ / -78°C  2. $H_2O_2$ / HO$^-$
w. Alkenes with Pd / H₂. Synthesis of “alkane” from “alkene” (hydrogenation). Simplistic mechanism:

Neutral metal atom can begin the process over = catalytic.

Hydride transfer also bonds carbon to the metal atom.

Syn (cis) addition of two hydrogens to the pi bond. Generally H₂ adds from the less sterically hindered face (i.e. the H₂ adds to the more open face).

Example reactions
x. Alkenes with Pd / D₂. Same hydrogenation reactions with deuterium from “alkene” (hydrogenation w/“D” = deuterium).
y. Alkynes with aqueous sulfuric acid (plus some Hg$^{2+}$ catalyst). Synthesis via enols (Markovnikov addition).

\[
\text{H}_2\text{SO}_4 / \text{H}_2\text{O} = \text{H}_3\text{O}^+ (\text{Hg}^{2+})
\]

Markovnikov addition (enol tautomerization to keto)

y. HX addition to alkynes. Markovnikov addition.

\[
\text{H-Br} \quad \text{or HCl or HI}
\]

Markovnikov addition
z. Bromination (or chlorination) of alkynes. Bridging bromonium ion.

\[
\begin{array}{c}
\text{Br}_2 \\
\text{or} \\
\text{Cl}_2 \\
\end{array} \quad \begin{array}{c}
\text{\textit{anti addition}}
\end{array}
\]

\[
\begin{array}{c}
\text{Br}_2 \\
\text{or} \\
\text{Cl}_2 \\
\end{array} \quad \begin{array}{c}
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\end{array}
\]

\[
\begin{array}{c}
\text{\textit{anti addition}}
\end{array}
\]

aa. 1. Hydroboration 2. oxidation of alkynes (anti-Markovnikov addition makes aldehydes or ketones via enolate).

\[
\begin{array}{c}
\text{HBR}_2 \\
1. \\
\text{H}_2\text{O}_2 / \text{HO} \\
\end{array} \quad \begin{array}{c}
\text{\textit{anti Markovnikov addition}}
\end{array}
\]

\[
\begin{array}{c}
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\[
\begin{array}{c}
\text{HBR}_2 \\
1. \\
\text{H}_2\text{O}_2 / \text{HO} \\
\end{array} \quad \begin{array}{c}
\text{\textit{anti Markovnikov addition}}
\end{array}
\]
bb. Catalytic hydrogenation reduces triple bond to “alkane”.

cc. Catalytic hydrogenation with quinoline “poison” of Pd catalyst reduces triple bond to Z alkene (syn addition).
dd. Sodium metal + liquid ammonia reduction of triple bond to E alkenes.

```
Na / NH₃
(liq - =33°C)
```

ee. Zipper reaction moves triple bond to terminal position where it can be removed to form sp carbanion nucleophile.

```
1. NaNR₂
2. WK
Zipper reaction
```

```
ff. Formation of conjugate base + addition of aldehyde electrophile forms propargyl alcohol.

\[
\begin{align*}
\text{1. } & \text{NaNR}_2 \\
\text{2. } & \text{O} \\
\text{H} \\
\end{align*}
\]


gg. Formation of conjugate base + addition of ketone electrophile forms propargyl alcohol.

\[
\begin{align*}
\text{1. } & \text{NaNR}_2 \\
\text{2. } & \text{O} \\
\text{H} \\
\end{align*}
\]
hh. Formation of conjugate base + addition of methyl or primary RX electrophile forms a longer alkyne.

ii. Formation of conjugate base + addition of secondary electrophile reacts in a nonproductive E2 reaction.
jj. Use zipper reaction to move alkyne through a linear chain to the end position. Work up 4 ways: a. with mild acid to generate the terminal alkyne, b. with an MeX or primary RCH2X to make a longer alkyne, c. with an aldehyde or ketone compound (C=O) or d. with an epoxide.

kk. Formation of conjugate base + addition of epoxide electrophile forms an alkynyl alcohol via S_N2 reaction.
II. Epoxides with terminal acetylides (followed by workup = neutralization).

mm. Epoxides with lithium diisopropyl amide (LDA, followed by workup = neutralization).
nn. Aldehydes and ketones with terminal acetylides.

owa. Aldehydes and ketones with secondary amines (enamine synthesis, alkylation, hydrolysis).