**Halogenation of Alkanes - Ch 4, 8**

- radical mechanism (write on back of card)
- only works with Cl₂ and Br₂
- usually results in multiple products
  - exceptions: when all carbons are the same (as above)
  - when one carbon forms a more stable radical (3°, benzyl, or allyl)

**E₂ Reaction of Alkyl Halides - Ch 8, 9**

- E₂ mechanism (write on back of card)
- only works with 2° and 3° alkyl halides
- with 2° alkyl halides, use (CH₃)₃COK to avoid S_N2 reactions
- must have a strong base (usually alkoxide)
- constitutional isomers may form if more than one β hydrogen is available
- anti elimination: when both carbons are stereocenters, only one stereoisomer is formed

**S_N2 Reaction of Alkyl Halides with Acetylide Anions - Ch 8, 11**

- S_N2 mechanism (write on back of card)
- alkyl halides must be 1° to avoid E2 reactions
- internal alkynes may be formed by using terminal alkynes which have been deprotonated with NaH or NaNH₂

**S_N2 Reaction of Alkyl Halides with Cyanide - Ch 8, 22**

- S_N2 mechanism (write on back of card)
- alkyl halides must be 1° to avoid E2 reactions
<table>
<thead>
<tr>
<th>ALKYL HALIDE</th>
<th>ALCOHOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_N^2$ Reaction of Alkyl Halides with Hydroxide - Ch 8, 12</td>
<td></td>
</tr>
<tr>
<td>![Reaction Diagram]</td>
<td></td>
</tr>
<tr>
<td>$\text{Br}^- \xrightarrow{\text{Na}^+ \cdot \text{OH}} \text{OH}^- + \text{Na}^+ \cdot \text{Br}^-$</td>
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</tr>
<tr>
<td>- $S_N^2$ mechanism (write on back of card)</td>
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<td>- alkyl halides must be $1^o$ to avoid E2 reactions</td>
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<tr>
<th>ALKYL HALIDE, ALCOHOL</th>
<th>ETHER</th>
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<tr>
<td>$S_N^2$ Reaction of Alkyl Halides with Alkoxides - Ch 8, 14</td>
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<td>![Reaction Diagram]</td>
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<tr>
<td>$\text{Br}^- \xrightarrow{\text{Na}^+ \cdot \text{O}} \text{O}^- + \text{Na}^+ \cdot \text{Br}^-$</td>
<td></td>
</tr>
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<td>- $S_N^2$ mechanism (write on back of card)</td>
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</tr>
<tr>
<td>- alkyl halides must be $1^o$ to avoid E2 reactions</td>
<td></td>
</tr>
<tr>
<td>- alkoxides are formed by reacting alcohols with NaH, Na (methyl, $1^o$) or K ($2^o$)</td>
<td></td>
</tr>
<tr>
<td>- $3^o$ alcohols cannot be used as they are too bulky to react in $S_N^2$ mechanisms</td>
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<tr>
<th>ALKENES</th>
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<td>Addition Reaction of HX to an Alkene - Ch 9</td>
<td></td>
</tr>
<tr>
<td>![Reaction Diagram]</td>
<td></td>
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<tr>
<td>$\text{HCl} \xrightarrow{\text{Cl}}$</td>
<td></td>
</tr>
<tr>
<td>- carbocation mechanism (write on back of card)</td>
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<td>- HCl, HBr, and HI may be used</td>
<td></td>
</tr>
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<td>- subject to rearrangements</td>
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<td>- halogen goes to the more substituted side of the C=C</td>
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<td>Addition Reaction of HX to an Alkene with Organic Peroxide - Ch 9</td>
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<td>![Reaction Diagram]</td>
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</tr>
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<td>$\text{HBr} \xrightarrow{\text{ROOR}} \text{Br}^-$</td>
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<tr>
<td>- radical mechanism (write on the back of card)</td>
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</tr>
<tr>
<td>- only HBr may be used (HCl, HI go by carbocation mechanism)</td>
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<td>- not subject to rearrangements</td>
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<td>- halogen goes to the less substituted side of the C=C</td>
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<tr>
<td>- all possible stereoisomers are formed</td>
<td></td>
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</table>
ALKENES → ALCOHOLS

**Acid Catalyzed Addition of Water to an Alkene - Ch 9**

- carbocation mechanism (write on back of card)
- acid is catalytic; it must have a non-nucleophilic conjugate base - phosphoric acid may also be used
- subject to rearrangements
- OH goes to the **more** substituted side of the C=C
- all possible stereoisomers are formed

**Addition of Water to an Alkene by Oxymercuration-reduction - Ch 10**

- reaction takes place in two steps
- not subject to rearrangements
- OH goes to the **more** substituted side of the C=C
- all possible stereoisomers are formed

**Addition of Water to an Alkene by Hydroboration-oxidation - Ch 10**

- reaction takes place in two steps
- only 1/3 equivalent of borane-THF is needed
- not subject to rearrangements
- OH goes to the **less** substituted side of the C=C
- H and OH are added to the same side (syn addition)

**Hydrogenation of an Alkene - Ch 10**

- excess hydrogen is always present (all C=C react)
- palladium is catalytic; other metals such as platinum or rhodium may be used
- the metal catalysts are pyrophoric (must be handled with care)
**ALKENE → VICINAL DIHALIDE**

Addition of \( X_2 \) to an Alkene - Ch 10, 11

\[
\text{alkene} + X_2 \rightarrow \text{vicinal dihalide}
\]

- bromonium ion mechanism (write on back of card)
- \( \text{Cl}_2, \text{Br}_2, \text{or} \text{I}_2 \) may be used
- not subject to rearrangements
- halogens added to opposite sides of the \( \text{C} = \text{C} \) (anti addition)

**ALKENE → HALOHYDRIN**

Addition of \( X \) and \( \text{OH} \) to an Alkene - Ch 10

\[
\text{alkene} + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{halohydrin}
\]

- bromonium ion mechanism (write on back of card)
- \( \text{Cl}_2, \text{Br}_2, \text{or} \text{I}_2 \) may be used
- not subject to rearrangements
- \( \text{OH} \) goes to the more substituted side of the \( \text{C} = \text{C} \)
- \( \text{OH} \) and \( X \) added to opposite sides of the \( \text{C} = \text{C} \) (anti addition)

**ALKENE → VICINAL DIOL**

Addition of \( \text{OH} \) to Both Sides of an Alkene - Ch 10

\[
\text{alkene} + \text{KMnO}_4 + \text{H}_2\text{O}, \text{NaOH} \rightarrow \text{vicinal diol}
\]

- product is also called a glycol
- \( \text{OsO}_4, \text{H}_2\text{O}_2 \) may also be used (fewer side reactions)
- not subject to rearrangements
- \( \text{OH} \)’s are added to the same side of the \( \text{C} = \text{C} \) (syn addition)

**ALKENE → ALDEHYDE, KETONE, or COOH**

Cleavage of an Alkene by Ozonolysis - Ch 10, 17, 20

\[
\text{alkene} + \text{O}_3 \rightarrow \text{aldehyde} + \text{keto} + \text{alkene} + \text{ozone}
\]

- formation of aldehyde or ketone depends on how many \( \text{C} \)’s are attached to each \( \text{C} \) of the \( \text{C} = \text{C} \)
- when hydrogen peroxide is used in place of dimethyl sulfide, aldehydes are oxidized to carboxylic acids
- cyclic alkenes give dicarbonyl compounds
- if both sides are identical, only one product is formed
ALKENE → CYCLOPROPANE
Addition of a Carbene to an Alkene to form a Cyclopropane - Ch 10

- reagents: 1) CH₂N₂ (diazomethane), heat
carbene mechanism (write on back of card)
2) CH₂I₂, Zn/Hg (Simmons-Smith reaction)
gives fewer side products
3) CHCl₃, (CH₃)₃COK
carbene mechanism (write on back of card)
two of the halogens remain attached
- not subject to rearrangements
- new carbon is added to the same side of the C= C
  (syn addition; "cis stays cis & trans stays trans")

ALKENE → EPOXIDE
Addition of Oxygen to an Alkene to form an Epoxide - Ch 10

- reagent is a peroxy acid and may be abbreviated PhCO₃H
- not subject to rearrangements
- oxygen is added to the same side of the C= C
  (syn addition; "cis stays cis & trans stays trans")

ALKENE → POLYMER
Addition of an Alkene to Another Alkene to form a Polymer - Ch 10

- reagents: 1) H₂SO₄
carbocation mechanism (write on the back of card)
2) ROOR, light or heat
radical mechanism (write on the back of card)
- carbocation mechanism is subject to rearrangements, radical
  mechanism is not
- all possible stereoisomers are formed

DIHALIDE → ALKYNE
Double Elimination of a Dihalide to form an Alkyne - Ch 11

- vicinal or geminal dihalides can be used in this reaction
- a much stronger base (NaNH₂) is needed for the elimination
  of the vinyl halide
- KOH may also be used if the temperature is increased to 200⁰K
- cumulated alkenes may form, but alkynes will predominate
- if a terminal alkyne is formed, water is needed to protonated the
  acetylide ion that forms in the prescience of the base
ALKYNE → CIS ALKENE
Hydrogenation of an Alkyne to form a Cis Alkene - Ch 11

\[
\text{H}_2 \quad \xrightarrow{\text{Lindlar}} \quad \text{cis-alkene}
\]

- Lindlar catalyst contains Pd/BaSO₄, quinoline and/or lead acetate
- H's are added to the same side of the triple bond
- only way to make the cis alkene exclusively

ALKYNE → TRANS ALKENE
Reduction of an Alkyne to a Trans Alkene - Ch 11

\[
\text{Na} \quad \xrightarrow{\text{NH}_3} \quad \text{trans-alkene}
\]

- radical mechanism (write on back of card)
- good way to make trans alkenes exclusively

ALKYNE → ALKANE
Hydrogenation of an Alkyne to an Alkane - Ch 11

\[
\text{H}_2 \quad \xrightarrow{\text{Pd/C}} \quad \text{alkane}
\]

- cannot be stopped at the alkene stage with these reagents

ALKYNE → VINYL HALIDE or DIHALIDE
Addition of 1 or 2 eq of HX to an Alkyne - Ch 11

\[
\text{alkyne} \quad \xrightarrow{\text{HBr}} \quad \text{vinyl halide} \quad \xrightarrow{\text{HBr}} \quad \text{dihalide}
\]

- HCl, HBr, and HI can be used
- halogen goes to the more substituted side of terminal alkynes unless ROOR is added
- both halogens are added to the same carbon
- anti addition is usually observed (X and H are trans)
**ALKYNE → VINYL DIHALIDE or TETRAHALIDE**

Addition of 1 or 2 eq of $X_2$ to an Alkyne - Ch 11

- $Cl_2$, $Br_2$, or $I_2$ may be used
- anti addition is usually observed ($X$'s are trans)

**ALKYNE → KETONE**

Addition of Water to an Alkyne (Hydration) - Ch 11

- $NaBH_4$ is not needed (unlike alkene reaction)
- an enol is initially formed; it tautomerizes to a ketone
- the OH (then C=O) goes to the **more** substituted side
- if the alkyne is not symmetrical, two products are formed

**ALKYNE → ALDEHYDE or KETONE**

Addition of Water to an Alkyne (Hydration) - Ch 11

1. $BH_3$
2. $H_2O_2$, NaOH

- terminal alkynes require a sterically hindered borane such as disiamyl borane or dicyclohexyl borane
- an enol is initially formed; it tautomerizes to a C=O the OH (then C=O) goes to the **less** substituted side
- terminal alkynes form aldehydes; internal alkynes form ketones
- if the alkyne is not symmetrical, two products are formed

**ALKYNE → DIKETONE**

Oxidation of an Alkyne to form a Diketone - Ch 11

- tetraol is initially formed; hydrates equilibrate to C=O's
- reaction must be kept cool and neutral, or the diketone may react further
Cleavage of an Alkyne by Ozonolysis - Ch 11

- no dimethyl sulfide or hydrogen peroxide is needed
- unsymmetrical alkynes give two products