<u>CHEM 261 Notes</u> <u>March 21, 2023</u>

RECALL:

Addition Reactions

- Occurs on double bonds and triple bonds

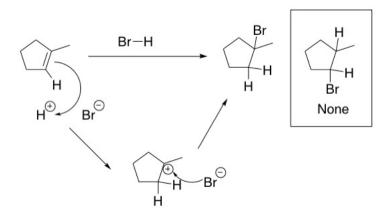
Hydrogen Halide (HX) Addition

- Reaction generally leads to syn/cis addition

Example 1: Ethylene

$$H_2C=CH_2$$
 H_2C-CH_2
 H
 Br
 H
 Br

Example 2: 1-Methylcyclopent-1-ene



- Markovnikov addition
- H⁺ would add to the less substituted C in the double bond to form the 3° carbocation (more stable due to alkyl stabilization inductive effect)

Example 3: Cyclobutene

Note: Need an acid (H⁺) to pull out the electrons from the double bond

Example 4: 1-Methylcyclohex-1-ene

RECALL: Carbocation stability 3° > 2° > 1° > CH₃+

Addition of H₂O and ROH (Hydration and Ether Formation)

Not Stereospecific

Hydration formation

- H₂O or ROH by itself cannot add to the double bond. Need an acid (H⁺) to pull the electrons from the double bond.
- H₂SO₄ (H⁺) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.

Example 1:

Example 2:

Ether formation

Example 1:

$$\begin{array}{c|c} & OH \\ \hline \\ H_2SO_4 \\ \end{array}$$
 an ether
$$\begin{array}{c} \\ + \\ \end{array}$$

Example 2:

Example 3:

Hydroboration

- B when stable and uncharged has 3 bonds and no lone pairs
- Borane forms partial bonds with another borane molecule to form B₂H₆ (diborane)
- Borane is a hydride (H⁻) donor

Fast and concerted

$$H_2C=CH_2$$
 $R=B$
 $H=B$
 $C=C$
 $C=C$
 $C=C$
 $R=B$
 R

Concerted reaction: bond breaking and bond formation happens in a single step **Anti-Markovnikov:** the hydrogen ends up on the more substituted C in a double bond.

Structure of borane

Exists as Diborane (B₂H₆), but behaves like BH₃

 BH_3

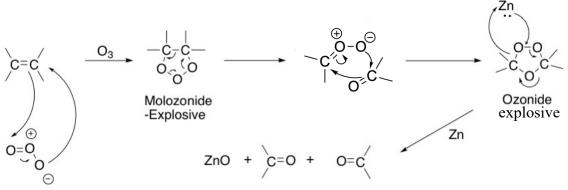
Borane

Example

Anti-Markovinkov

Ozonolysis (lysis = cleavage) – cleavage by ozone (O_3)

- Use double-headed arrow to indicate resonance (\leftrightarrow)
- Highly reactive (always looking for negative charge such as the negative charge in a double bond)
- Concerted and stereospecific



- Reaction is irreversible

Examples of carbonyl groups

Reaction scheme of ozone

$$c=c$$
 $1. O_3$ $c=0$ $c=0$

Example

$$C=CH_2$$
 $1. O_3$
 $2. Zn$
 $C=O$
 $O=C$
 H
 O
 H
formic acid (from ants)

More examples

Epoxidation:

Syn/Cis Addition Stereospecific

Concerted (bonds break and form at the same time)

Mechanism:

Example 1: trans- vs cis-Butene

The possibility of epoxidation from the top is 50% and from the bottom is 50% so a 1:1 mixture of enantiomers is form (racemic mixture).

Enantiomers

Racemic mixture

Example: 1-methyl-1-cyclohexene

Racemic mixture (1:1) cis/syn addition

Example 2: 2-Methyl-7-octadecene

biologically, only one enantiomer is active (one shown) - racemate produced by peracetic acid

Example 3:

