Helpful overview of alkene nucleophilic reactivity (with regioselectivity and diastereoselectivity info)
Alkenes as Nucleophiles

\[ \text{E-Nuc (e.g., H-Br)} \rightarrow \text{Product} \]

Mechanism:

1. **Reagents**
2. **Regioselectivity** (Mark vs. Anti-Mark)
3. **Potential diastereoselectivity** (syn vs. anti)
4. **Potential carbocation rearrangement** (alkyl or hydride shifts)
42) Predict the major product(s) for each of the following reactions:

- **[3+2]** reaction followed by syn dihydroxylation.

- Hydrohalogenation with Markovnikov selectivity.

- Full addition with anti di-bromination.
\[ \text{Hg(OAc)}^* \] forms H bonds on surface (heterogeneous catalysis)

*from \( \text{Hg(OAc)}_2 \) dissociation

\[ \text{NaBH}_4 \]
44) Propose a mechanism for each of the following reactions:

(a) \[\text{propene} + H_2O^+ \rightarrow \text{propyl alcohol}\]

(b) \[\text{propene} + H_2O^+ \rightarrow \text{propyl alcohol}\]

(c) \[\text{propene} + HBr \rightarrow \text{propyl bromide}\]

(d) \[\text{propene} + HBr \rightarrow \text{propyl bromide}\]
c) 

\[ \text{most stable carbocation} \]

(3)

(3) 

(2)

alkyl shift to make more stable carbocation

d)
52) Suggest suitable reagents to perform each of the following transformations:

1. \[ \text{ROOR, } H-\text{Br} \rightarrow mCPBA \]
2. \[ H-\text{Br} \]
3. \[ H_{3}O^{+} \]
4. \[ 1) BH_{3} \cdot THF \quad 2) \text{H}_{2}O_{2}, \text{NaOH} \]
53) (R)-Limonene is found in many citrus fruits, including oranges and lemons:

\[ \text{H}_2 \quad \text{eg. Pt or Pd/C} \]

Draw the structures and identify the relationship of the two products obtained when (R)-limonene is treated with excess hydrogen in the presence of a catalyst.

Cis and trans diastereomers!
57) Predict the major product(s) for each of the following reactions:

(a) \[ \text{H}_2 \quad \text{(PPh}_3\text{)RhCl} \] \[ \text{?} \] syn hydrogenation (homogeneous catalysis)

(b) \[ \text{H}_2\text{O}^+ \] \[ \text{?} \] Markovnikov hydration

(c) \[ \text{1) BH}_3 \text{+ THF} \quad \text{2) H}_2\text{O}_2, \text{NaOH} \] \[ \text{?} \] Anti-Markovnikov hydration

(d) \[ \text{1) RCO}_2\text{H} \quad \text{2) H}_2\text{O}^+ \] \[ \text{?} \] Anti dihydroxylation (through epoxide as an intermediate) similar to halonium + mercurium int. seen before

Mechanism for (d):

\[ \text{EPOXIDE INT.} \] \[ \text{+enam} \]

\[ \text{H}_2\text{O} \] \[ \text{+enam} \]
83) When 3-bromocyclopentene is treated with HBr, the observed product is a racemic mixture of trans-1,2-dibromocyclopentane. None of the corresponding cis-dibromide is observed. Propose a mechanism that accounts for the observed stereochemical outcome:

*Reactions using HBr are not usually diastereoselective (anti vs. syn selectivity)*

Remember: dibromination using Br₂ also gives the anti product (result of the bromonium intermediate)