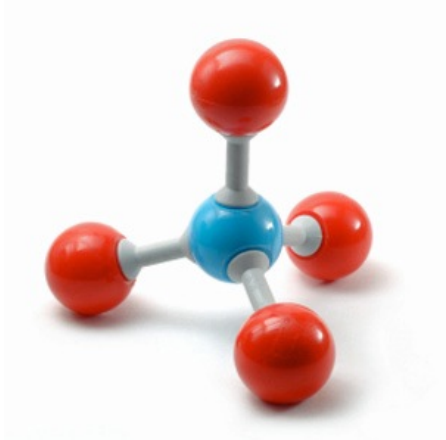
Ch14

Selectivity

Considering specificity and selectivity
in converting functional groups.



version 1.0

Ch14

Selectivity in Organic Reactions

- Writing chemical equations
  - Knowing a chemical reaction
    - Distinguishing between specificity and selectivity
  - Specificity
    - What changes <u>will</u> (or will not) occur, if the rxn happens
  - Selectivity
    - When more than one thing can happen in a reaction, there <u>may</u> be selectivity (favoring one choice)
      - Regio selective – what areas of the molecule does the reaction favor?
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    - We may talk about another kind later in the term
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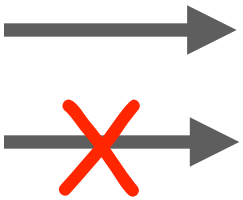
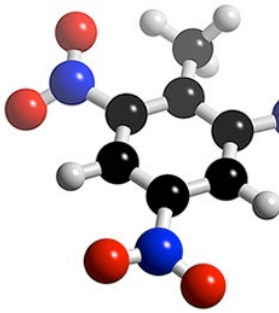
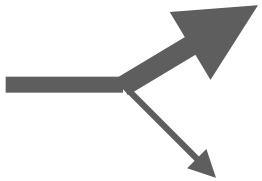
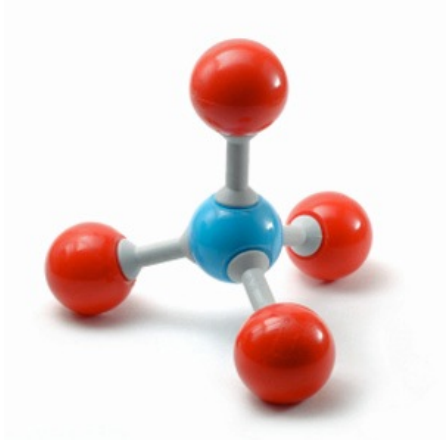
  - Examples









Writing Chemical Equations

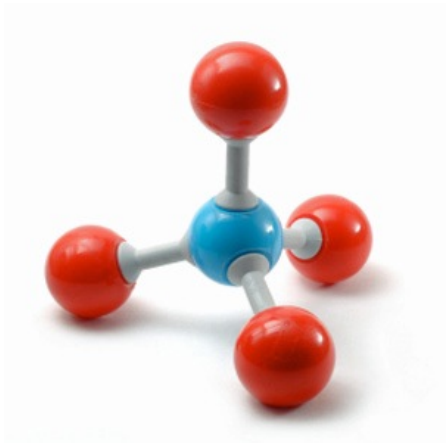
- Chemical equations are an attempt to express all the relevant observations of a chemical change in a concise but complete form.
- You want to include:
  - All reactants
  - All products
  - Any significant conditions
- You're used to expressing the participants in a chemical reaction using molecular formulas.

Exp #1:

$$C_5H_{10} + H_2 \xrightarrow{\text{Ni or Pd or Pt}} C_5H_{12}$$

Exp #2:

$$C_5H_{10} + O_2 \xrightarrow{\text{HEAT}} CO_2 + H_2O$$



Writing Chemical Equations

- You're used to expressing the participants in a chemical reaction using molecular formulas.
- Organic molecules have greater complexity.
- Their identity does not depend only on composition, a molecular formula is not enough to differentiate between substances.
- Connectivity and sometimes Shape need to be expressed.

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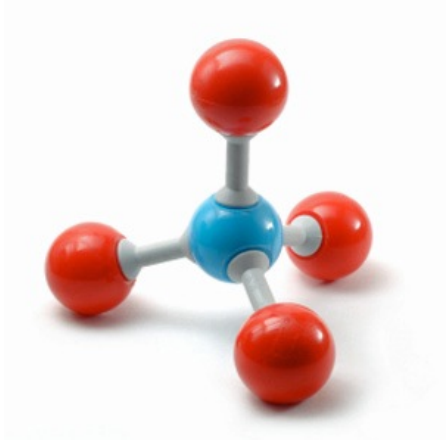
$$C_5H_{10} + H_2 \xrightarrow{\text{Ni or Pd or Pt}} C_5H_{12}$$

Exp #2:

$$C_5H_{10} + H_2 \xrightarrow{\text{Ni or Pd or Pt}} \text{N/R}$$



Writing Chemical Equations

- You're used to expressing the participants in a chemical reaction using molecular formulas.
- Organic molecules have greater complexity.
- Their identity does not depend only on composition, a molecular formula is not enough to differentiate between substances.
- Connectivity and sometimes Shape need to be expressed.
- We substitute molecule structures for molecular formulas in most organic equations to provide that greater clarity.

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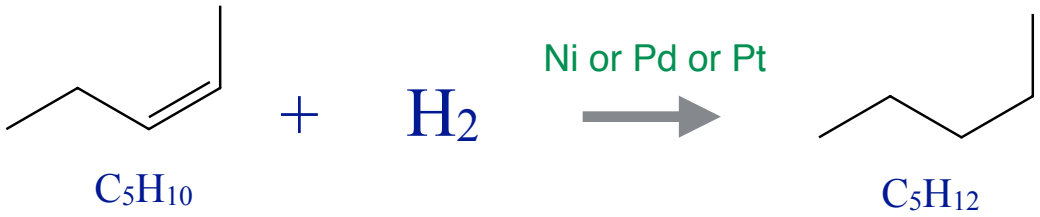
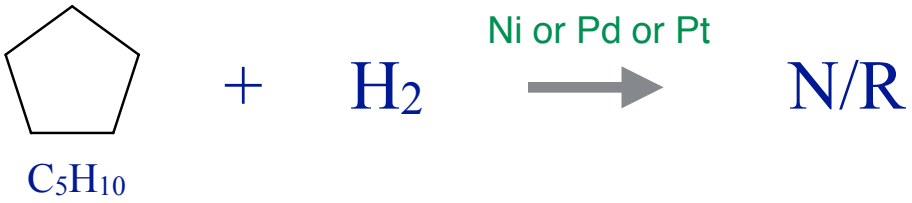
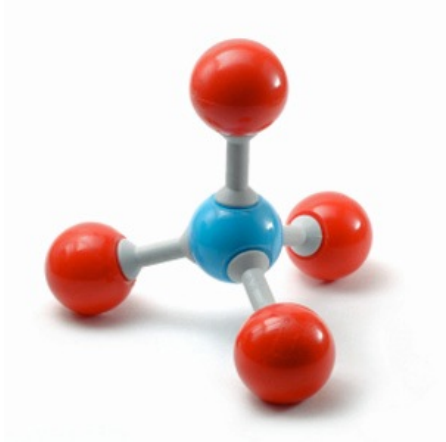


Exp #2:





Ch14

Selectivity in Organic Reactions

- Writing chemical equations
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  - Distinguishing between specificity and selectivity
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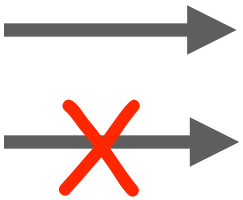
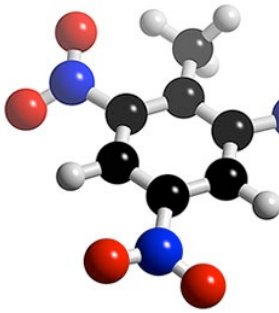
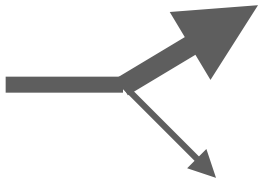
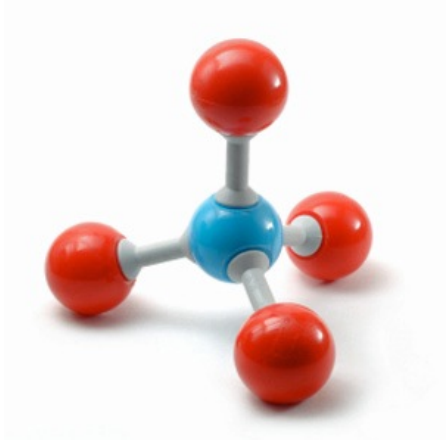


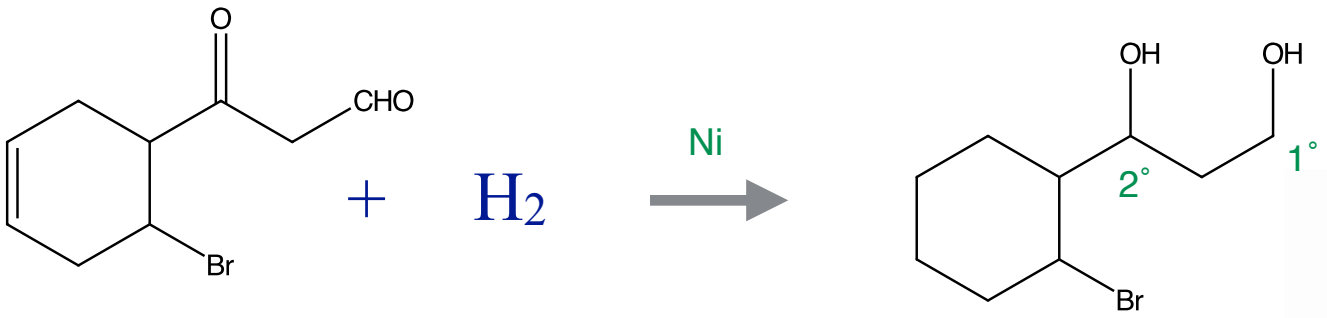


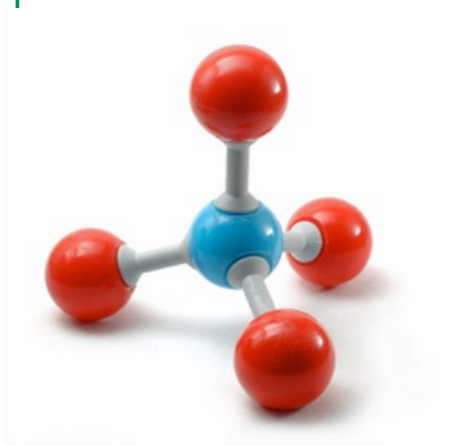




Specificity & Selectivity

- As structures become more involved, more chemical changes are possible.
- For a reaction to be useful, we need to be able to predict the extent and limit of those changes.
- Understanding organic reactions means knowing their specificity and their selectivity.
  - We need to know what **specific** alterations the reaction accomplishes.
  - Where the reaction can do more than one thing, we need to understand how one region of the molecule, functional group, or stereoisomer might be **selected** over another.





Ref: Selectivity and specificity in organic reactions, Addison Ault, J. Chem. Educ., 1977, 54 (10), p 614
DOI: 10.1021/ed054p614

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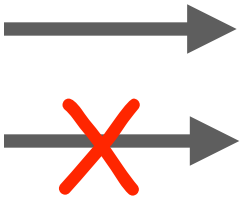
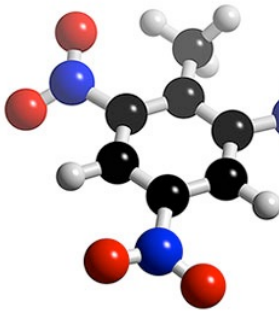
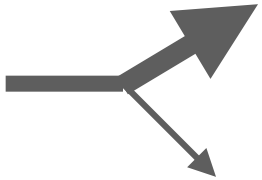
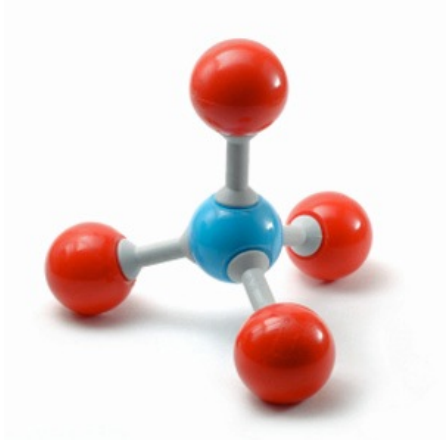


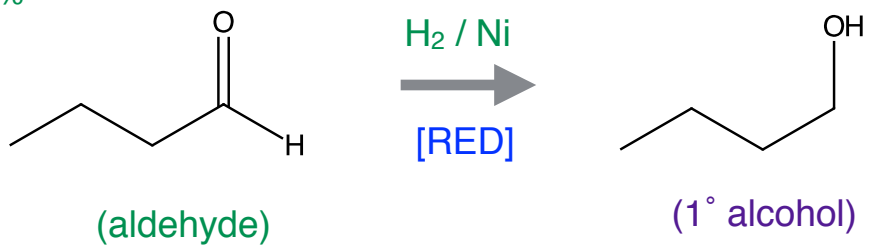




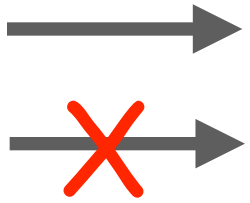


Specificity

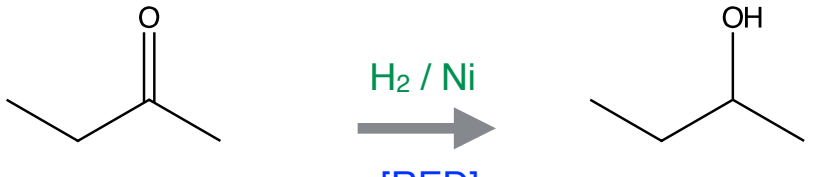
- Specificity describes the chemical changes that define the reaction.
  - Knowing the specifications of a chemical reaction, is knowing that reaction.
  - The specificity is what we can count on — it's the change that never varies.
- Specificity is inherent in the reaction mechanism.
- Reduction of a carbonyl with raney nickel and hydrogen gas is specific in the following results.
  - Aldehydes specifically form primary alcohols.
    - Always, 100%



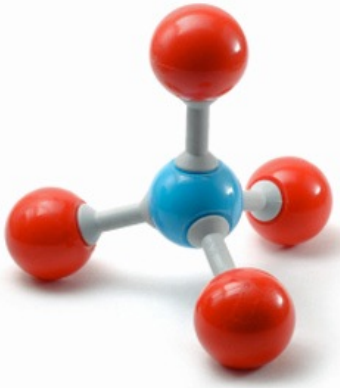
(aldehyde) (1° alcohol)



  - Ketones specifically form secondary alcohols.
    - Always, 100%



(ketone) (2° alcohol)



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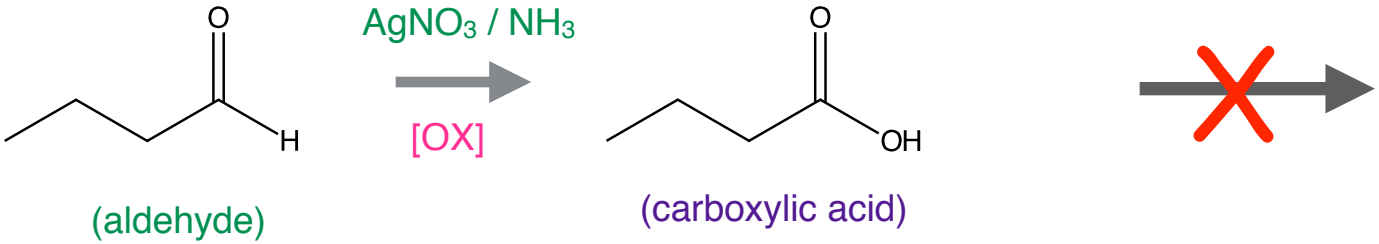
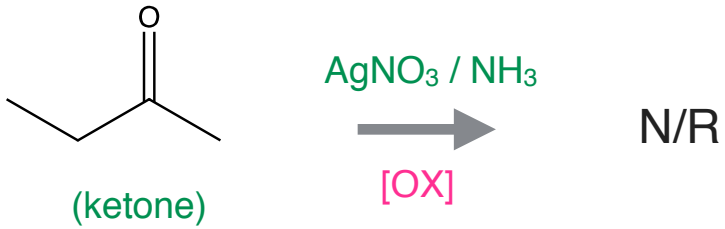
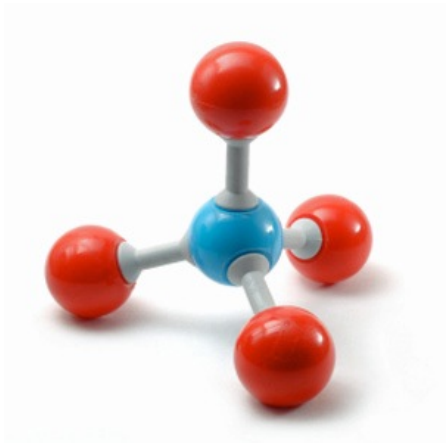
  - Knowing the specifications of a chemical reaction, is knowing that reaction.
  - The specificity is what we can count on — it's the change that never varies.
- If the specific change doesn't occur N/R happens.
- Oxidation of a carbonyl with silver nitrate is specific in the following results.
  - Aldehydes specifically form carboxylic acids.
    - Always, 100%



  - Ketones do not react.
    - Always, 100%





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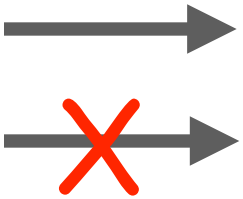
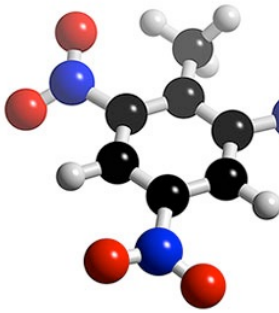
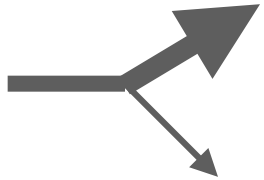
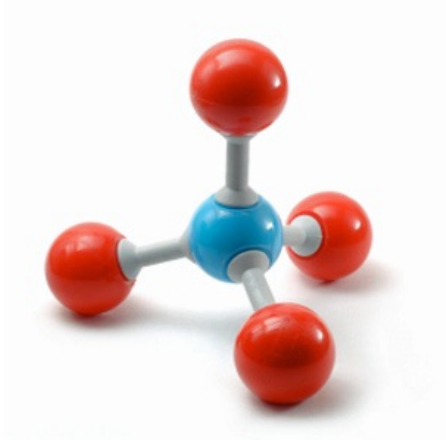


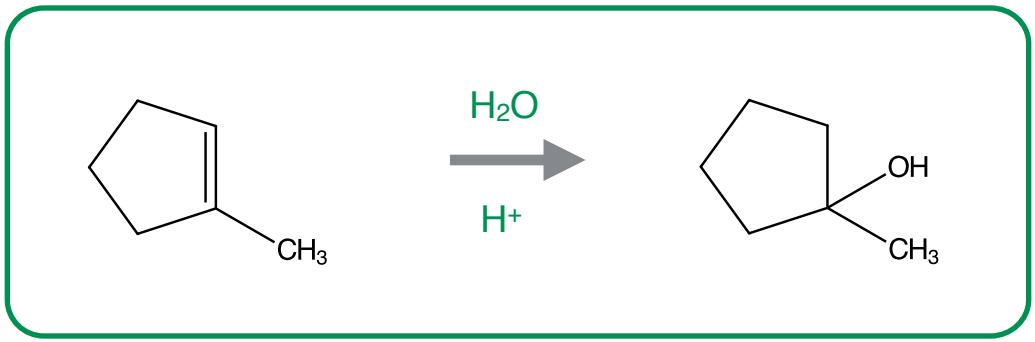


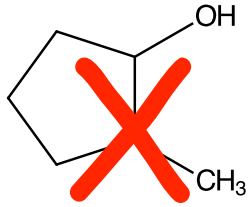


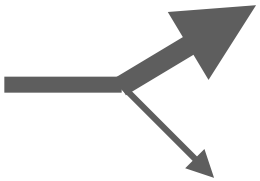


Regioselectivity

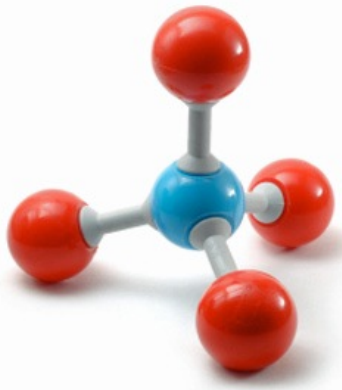
- Some reactions can occur in more than one way. (not all reactions, but some)
- Selectivity describes the preferred changes when multiple changes are possible.
  - Knowing the selectivity in a chemical reaction, let's you predict that choice.
  - Knowing selectivity allows you to use the reaction in more complex systems.
- In some reactions, the change can occur in more than one region of the molecule.
- Regioselectivity describes the preference for one structural isomer over another.







- Hydration reactions have a regioselectivity for placing the alcohol on the more substituted carbon in a double bond.



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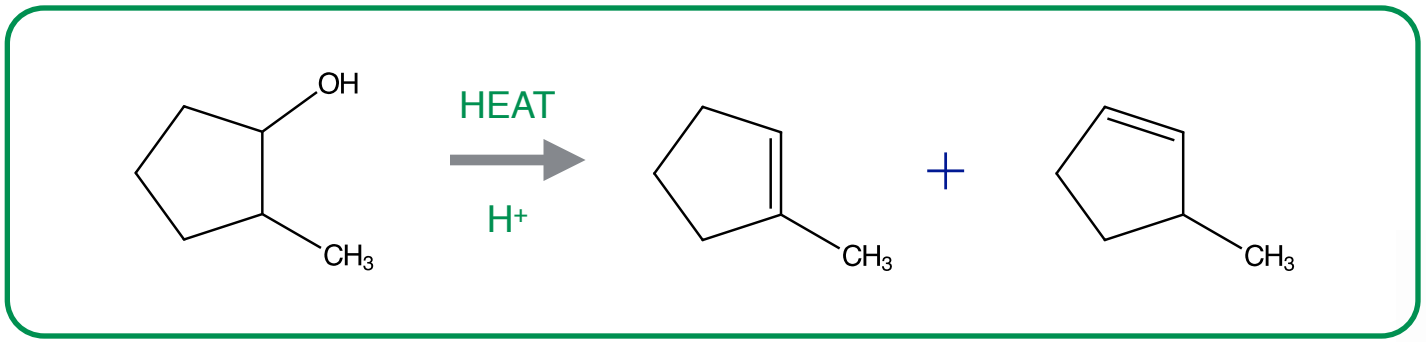
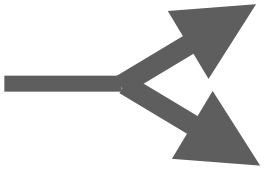
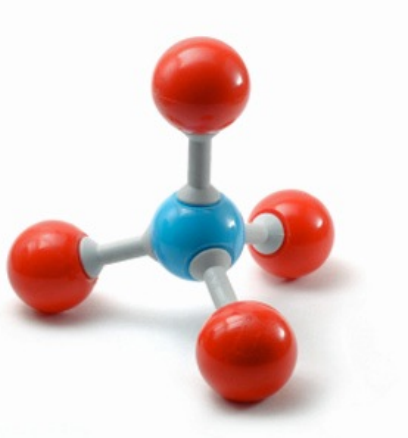




- Elimination of alcohols does not have regioselectivity as to which side of the alcohol the double bond forms (or poor selectivity).
- You must show both products produced.



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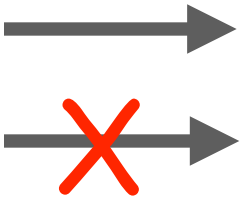

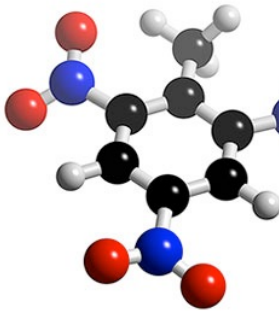

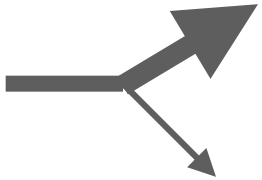

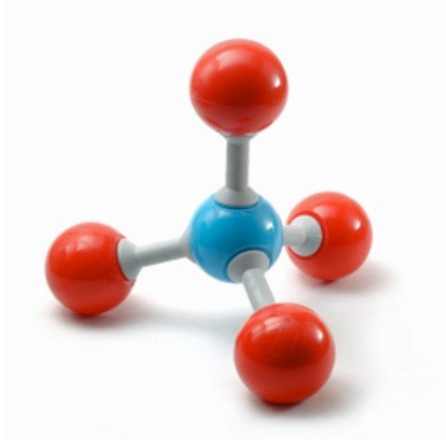

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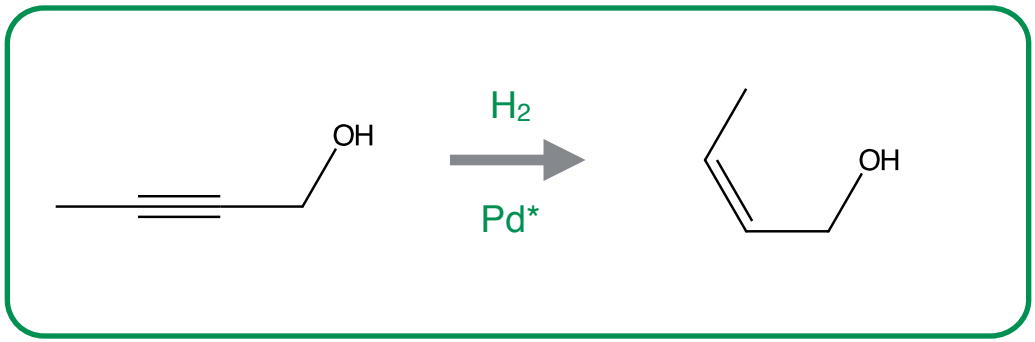

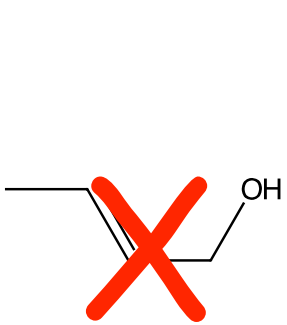

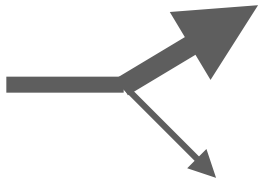

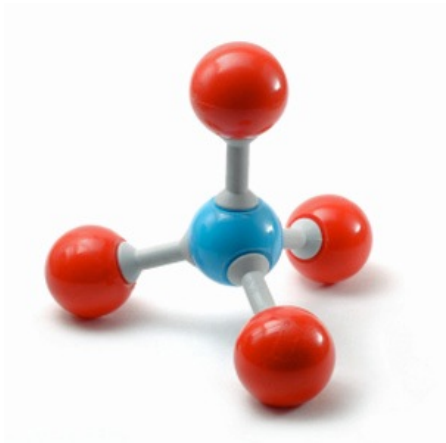

- Hydrogenation reactions of alkynes with certain Lindlar's Catalyst stereoselectively form cis alkenes — not trans alkenes.

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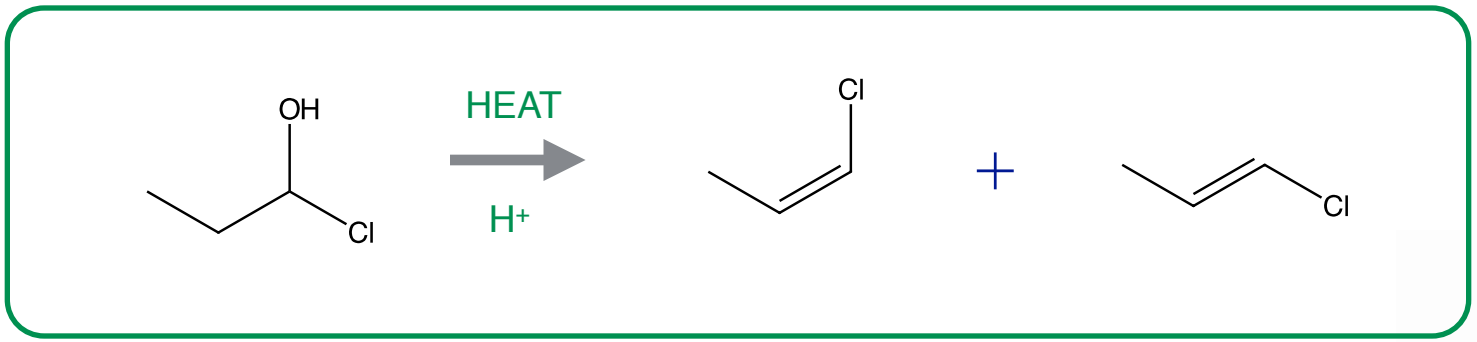
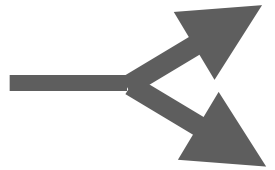
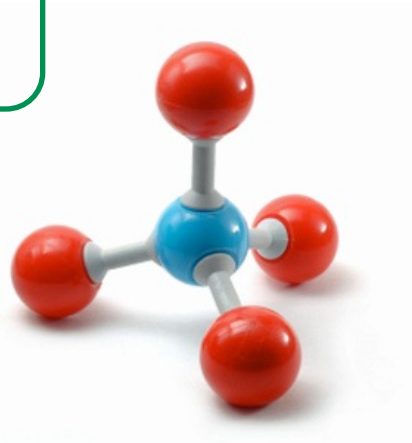
- In some reactions, the change can produce more than one stereoiosomer.
- Stereoselectivity describes the preference for one stereoisomer over another.





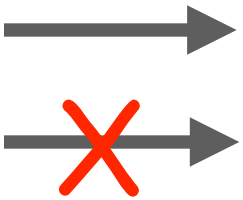
- Elimination of alcohols does not have stereoselectivity as to which double bond forms (cis or trans).
- You must show both products produced.

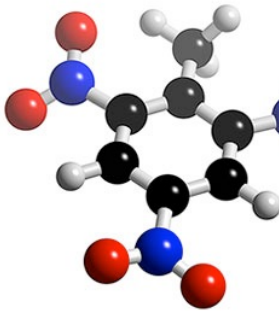


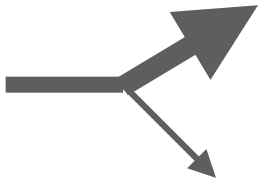
Ch14

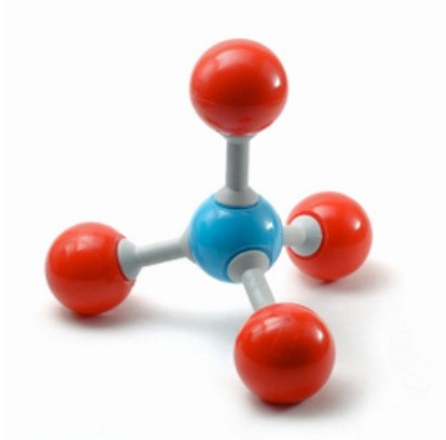
Selectivity in Organic Reactions

- Writing chemical equations
- Knowing a chemical reaction
  - Distinguishing between specificity and selectivity
- Specificity
  - What changes <u>will</u> (or will not) occur, if the rxn happens
- Selectivity
  - When more than one thing can happen in a reaction, there <u>may</u> be selectivity (favoring one choice)
    - Regio selective – what areas of the molecule does the reaction favor?
    - Stereo selective – what stereochemistry does the reaction favor?
  - We may talk about another kind later in the term
    - Group selective – what groups in the molecule does the reaction favor?
- Examples

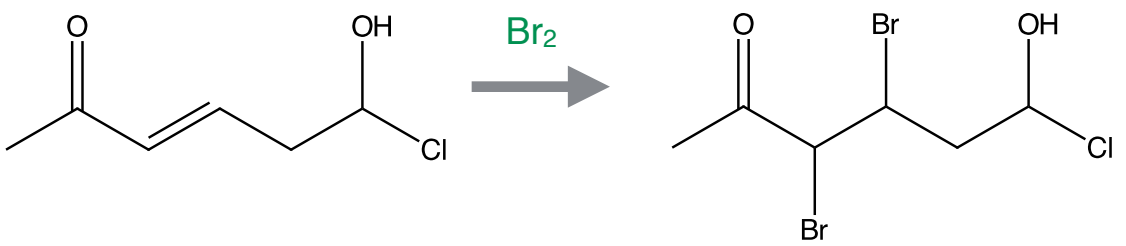




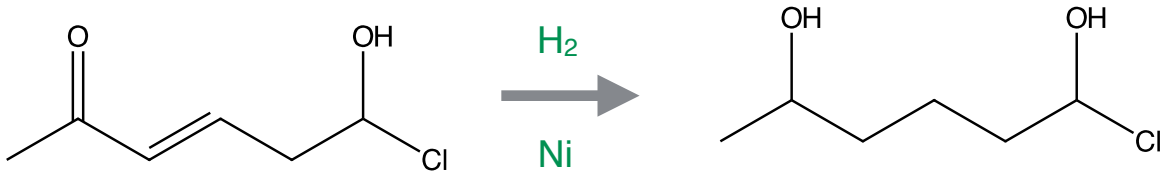




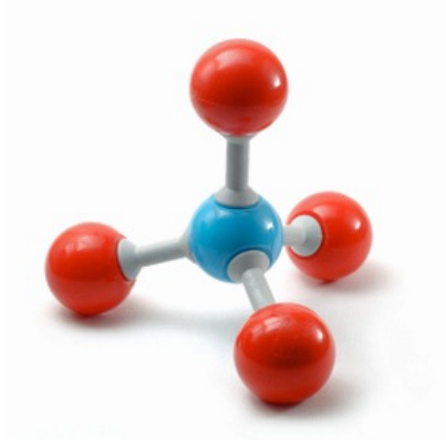
Examples, Specificity



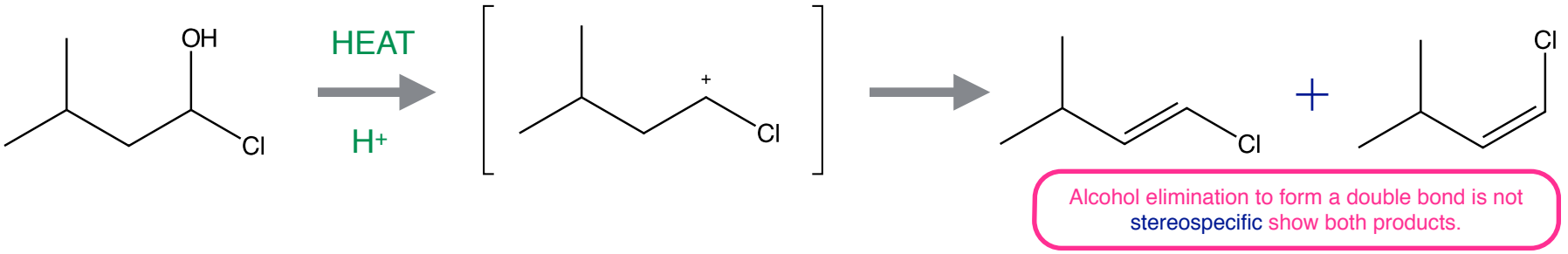
Bromine addition is specific to double bonds.



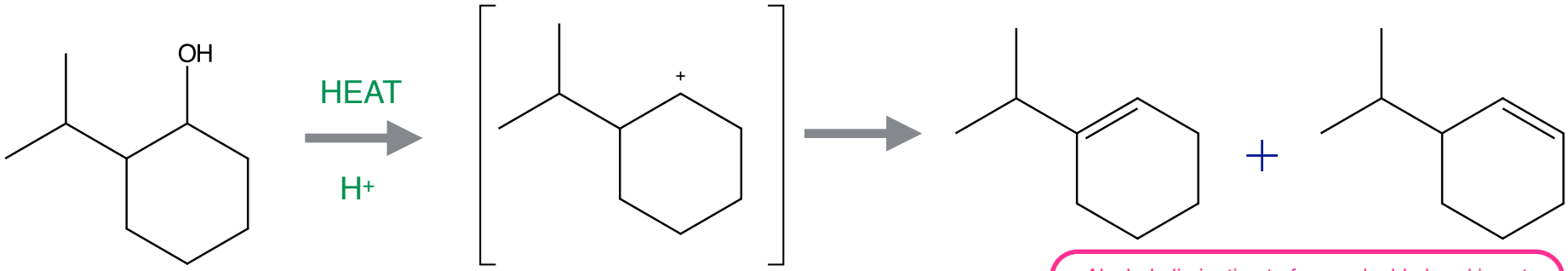
Hydrogen addition is not specific between double bonds and carbonyls.



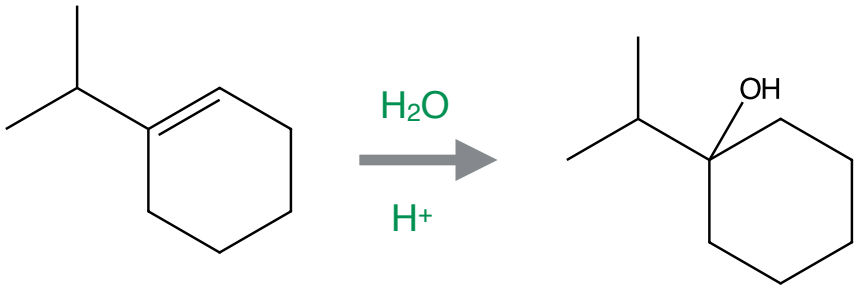
Examples, Selectivity



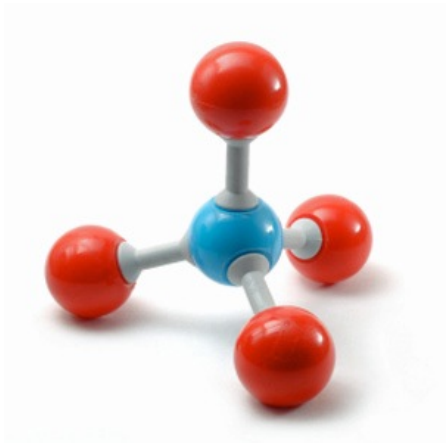
Alcohol elimination to form a double bond is not stereospecific show both products.



Alcohol elimination to form a double bond is not regioselective show both products.



Alcohol addition to a double bond is regioselective show the selected product.



Questions?