CHEMISTRY 2500

Topic #6: Reaction Types and Factors Favouring Reactions

Fall 2014

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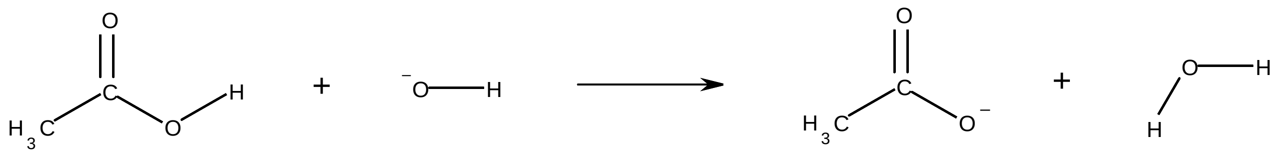
Reaction Types in Organic Chemistry

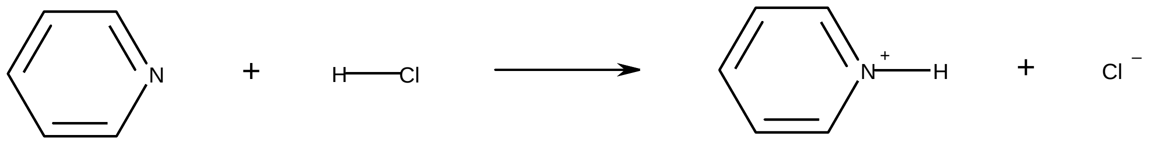
- The vast majority of reactions in organic chemistry can be grouped into a short list of categories:
  - proton-transfer reactions
  - substitution reactions
  - addition reactions
  - elimination reactions
  - oxidation reactions
  - reduction reactions
  - rearrangements

Reaction Types: Proton-Transfer Reactions

- Proton-transfer reactions are Brønsted acid-base reactions. H^+ is transferred from an acid to a base.

  e.g.



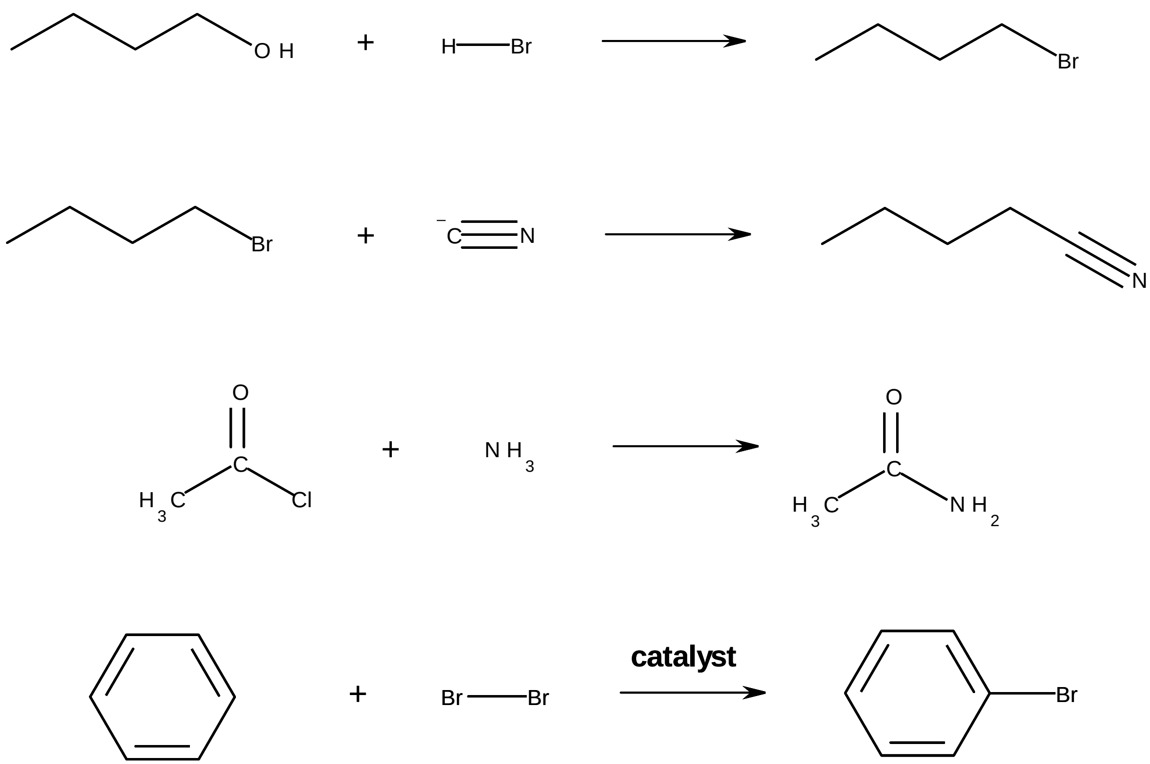


Fill in the missing lone pairs and use “curly arrows” to show the movement of electrons for the two reactions shown above.

Reaction Types: Substitution Reactions

- Substitution reactions are reactions in which an atom or group from the organic reactant is replaced by a different atom/group.

e.g.

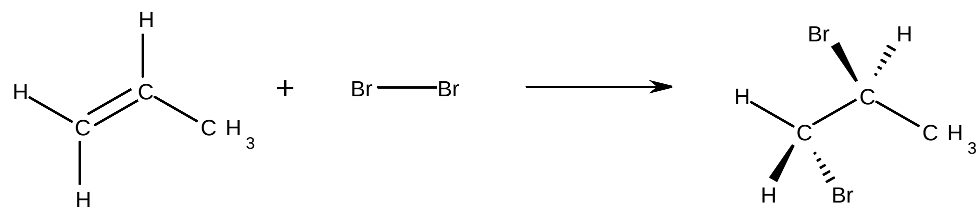


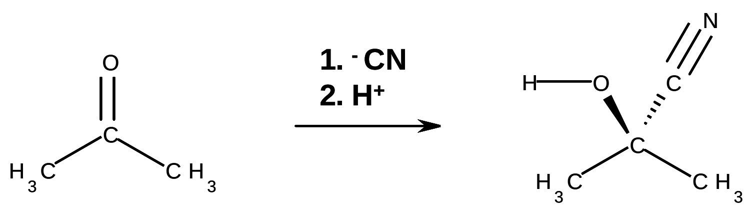
Fill in the missing lone pairs and balance each chemical equation. Also, circle the atoms/groups involved in the substitution.

Reaction Types: Addition Reactions

- Addition reactions are reactions in which a π bond is broken, allowing two groups to be added to a molecule (one new bond to each atom that used to be part of the π bond).
- These two groups are often, but not always, two "halves" of a small molecule. *(As you will see later, the H^+ and ^-OH for "addition of H_2O" usually come from two different molecules.)*

e.g.



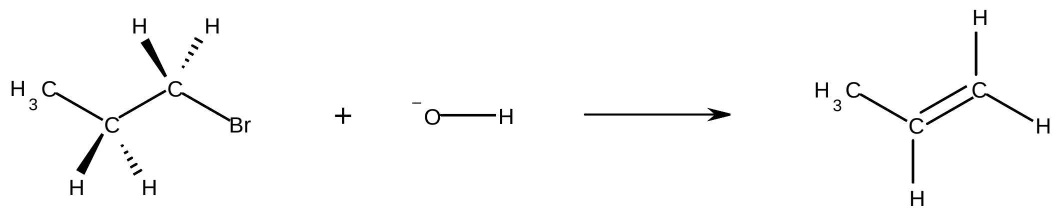


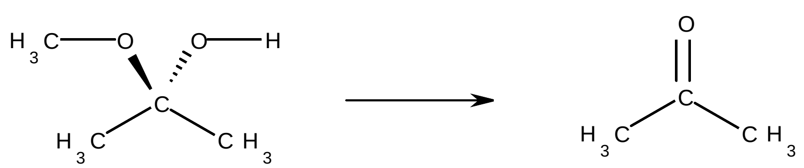
Fill in the missing lone pairs and count the bonds around each atom involved in the reaction to confirm that the octet rule is not violated.

Reaction Types: Elimination Reactions

- Elimination reactions are reactions in which a π bond is formed by removal of two groups from a molecule. *(In many cases, an elimination reaction and an addition reaction are the forward and reverse directions for the same equilibrium.)*

e.g.



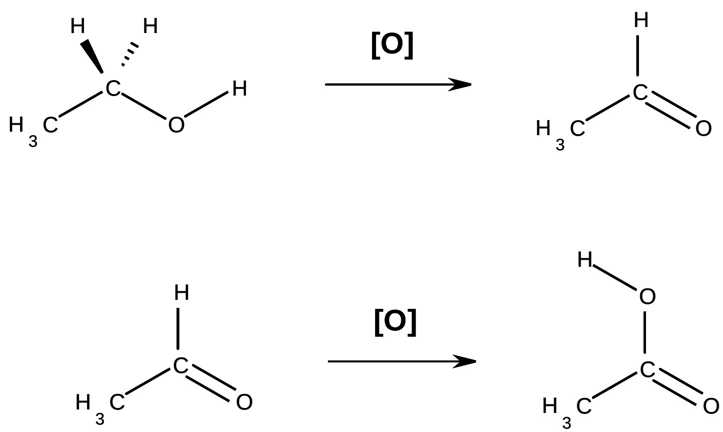


Fill in the missing lone pairs and balance each chemical equation. Count the bonds around each atom involved in the reaction to confirm that the octet rule is not violated.

Reaction Types: Oxidation Reactions

- As you know from CHEM 2000, nothing can be oxidized without something else being reduced. In organic chemistry, an oxidation reaction is a reaction in which the organic reactant is oxidized (while another reactant, often inorganic, is reduced).
- Oxidation reactions can usually be recognized by the gain of oxygen or loss of hydrogen (or both) from the organic reactant.

e.g.

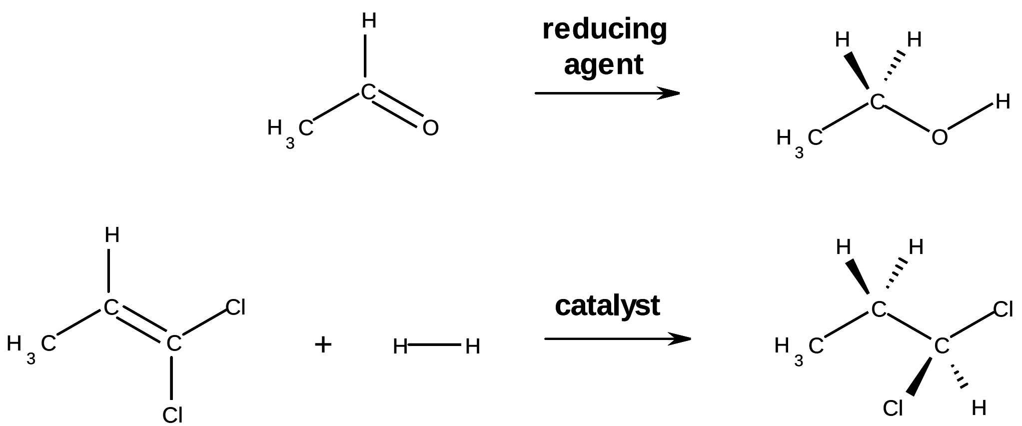


Fill in the missing lone pairs and determine the oxidation state of each carbon atom to confirm that electrons were lost.

Reaction Types: Reduction Reactions

- As you know from CHEM 2000, nothing can be reduced without something else being oxidized. In organic chemistry, a reduction reaction is a reaction in which the organic reactant is reduced (while another reactant, often inorganic, is oxidized).
- Reduction reactions can usually be recognized by the loss of oxygen or gain of hydrogen (or both) from the organic reactant.

  e.g.

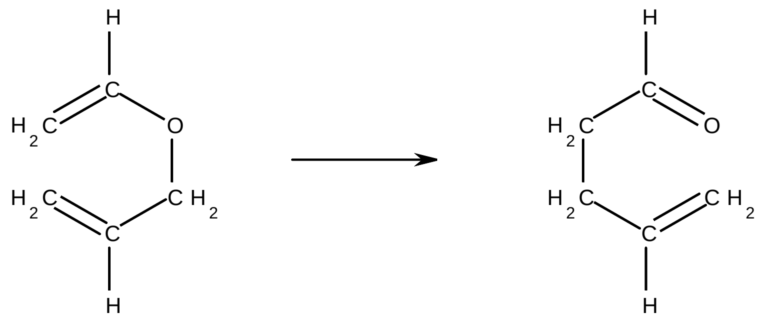


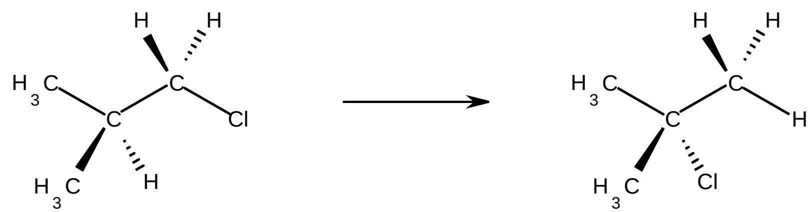
Fill in the missing lone pairs and determine the oxidation state of each carbon atom to confirm that electrons were gained.

Reaction Types: Rearrangement Reactions

- Rearrangement reactions are reactions in which no atoms are lost or gained from a molecule; they are simply rearranged. In other words, the product is an isomer of the reactant.

e.g.

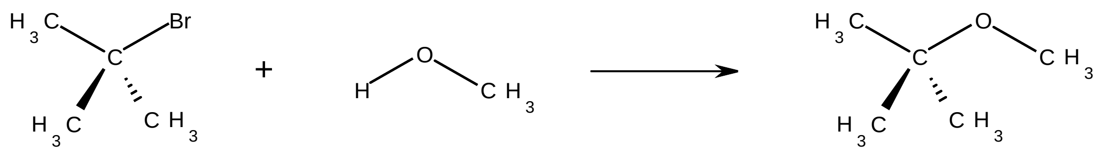


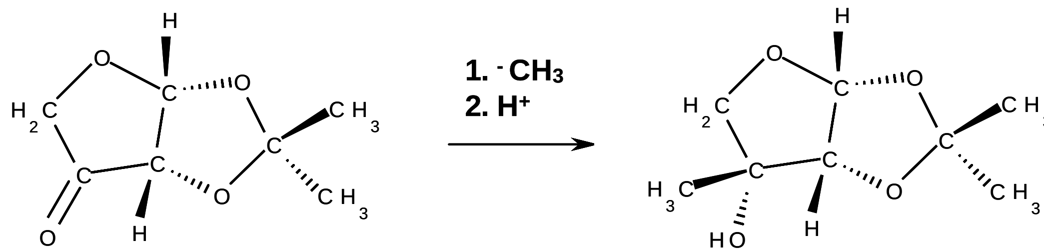


Fill in the missing lone pairs and indicate the stereochemical relationship between reactant and product.

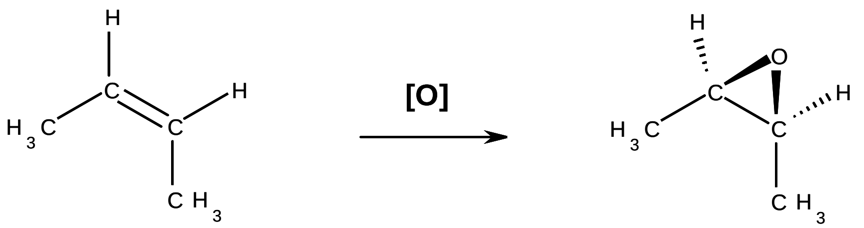
Reaction Types: Practice

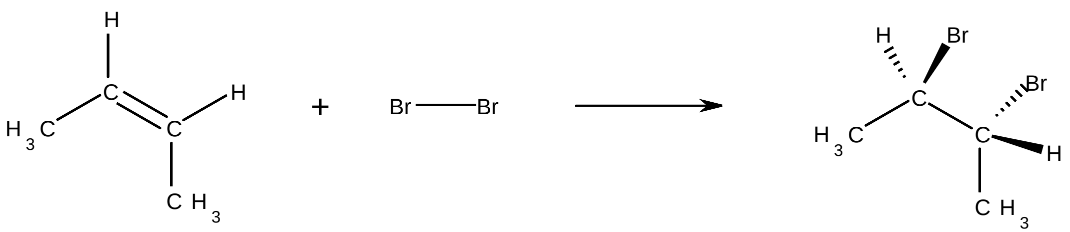
- Classify each of the following reactions as a proton-transfer, substitution, addition, elimination, oxidation, reduction or rearrangement reaction. It is possible that some reactions will belong to two categories... Briefly justify your choice, then fill in the missing lone pairs and balance any equation that is not an oxidation or reduction reaction.

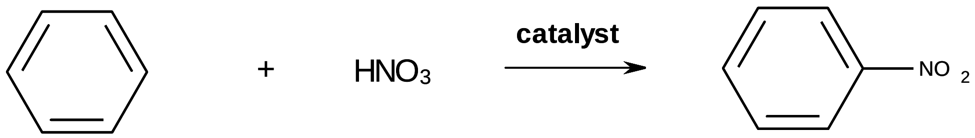




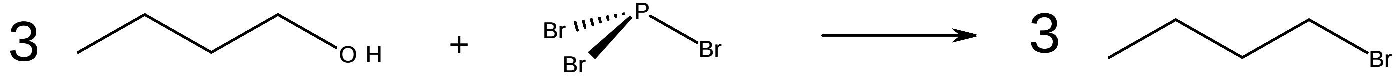
Reaction Types: Practice

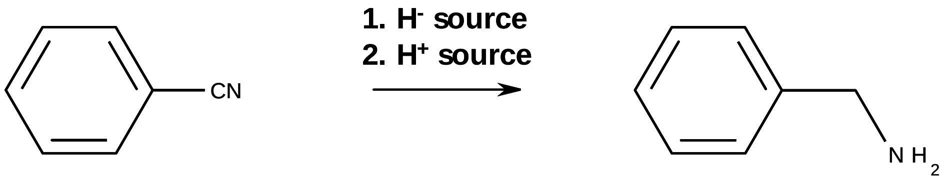






Reaction Types: Practice





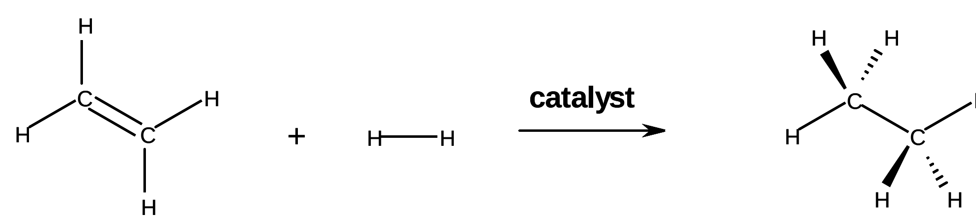
Organic Reactions: Why do they Proceed?

- Organic reactions are no different from any other kind of chemical reaction. In order to proceed, they must be favourable both kinetically and thermodynamically:
  - Kinetics: If the activation energy for a reaction is too high, the reaction will not proceed. This can sometimes be overcome by supplying energy to the system (e.g. heating) or by providing a catalyst that allows the reaction to proceed via a different path with a lower activation energy:

Organic Reactions: Why do they Proceed?

- Thermodynamics: In order for a reaction to proceed, it **must** have a negative Gibbs Free Energy under the reaction conditions. This is a direct consequence of the Second Law of Thermodynamics since $\Delta G = -T\Delta S_{universe}$ and the entropy of the universe cannot decrease.
- Whether the Gibbs Free Energy for a reaction will be positive or negative can be predicted by looking at the sign of the enthalpy change and the entropy change since $\Delta G = \Delta H - T\Delta S$
  - A reaction is favoured by enthalpy if heat is produced ($\Delta_r H<0$). The enthalpy change for a reaction can be approximated using the bond energies*: $\Delta_r H \approx \Sigma\Delta_{BD}H_{bonds\text{-}broken} - \Sigma\Delta_{BD}H_{bonds\text{-}formed}$

    So, if stronger bonds are formed than were broken, ΔH will be negative:



$$\Delta H \approx (\Delta_{BD}H_{C=C} + \Delta_{BD}H_{H\text{-}H}) - (\Delta_{BD}H_{C\text{-}C} + 2\ \Delta_{BD}H_{C\text{-}H})$$

$$\Delta H \approx (611\ \text{kJ/mol} + 437\ \text{kJ/mol}) - (347\ \text{kJ/mol} + 2\times 414\ \text{kJ/mol})$$

$$\Delta H \approx -127\ \text{kJ/mol}$$

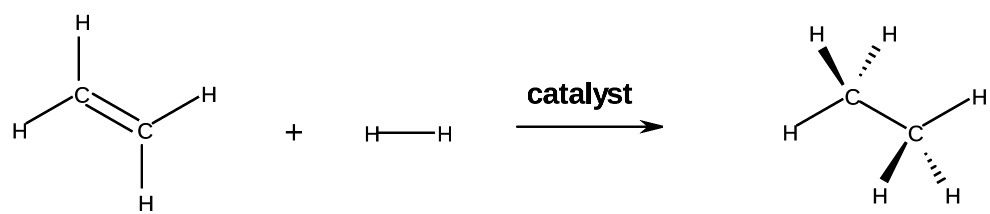
*A "bond energy" is the enthalpy change for breaking that bond. It is more properly termed "enthalpy of bond dissociation" ($\Delta_{BD}H$).

Organic Reactions: Why do they Proceed?

- A reaction is favoured by entropy if the entropy of the sytem increases ($\Delta_r S>0$). Whether the entropy of the system increases or decreases can be predicted by looking at the gaseous reactants and products. Since gases have much higher entropies than solids and liquids, a reaction which increases the number of gas molecules in the system will tend to have $\Delta_r S>0$ while a reaction that decreases the number of gas molecules in the system will tend to have $\Delta_r S<0$.

  For each of the reactions below, indicate whether or not it is favoured by entropy?

$$CH_3OH_{(l)} + SOCl_{2(l)} \longrightarrow CH_3Cl_{(g)} + SO_{2(g)} + HCl_{(g)}$$



Organic Reactions: Why do they Proceed?

- A reaction which is favoured by both enthalpy and entropy will clearly be thermodynamically favoured ($\Delta_r G<0$).
- A reaction which is not favoured by either enthalpy or entropy will clearly not be thermodynamically favoured ($\Delta_r G>0$).
- Reactions which are favoured by one factor but not the other will sometimes be thermodynamically favoured. At this point, we have to look at temperature to determine which factor dominates. Since $\Delta G = \Delta H - T\Delta S$, ___________________________ dominates at high temperatures while ________________________ dominates at low temperatures.
- In summary:
  - If ΔH is + and ΔS is –, reaction is ________________________
  - If ΔH is – and ΔS is +, reaction is ________________________
  - If ΔH is + and ΔS is +, reaction is ________________________
  - If ΔH is – and ΔS is –, reaction is ________________________
- A reaction which is never favoured is a reaction which you will not see in this course. Since it doesn't happen.

Organic Reactions: Why do they Proceed?

- Consider the seven categories of organic reactions we looked at earlier in the notes:
  - proton-transfer reactions
  - substitution reactions
  - addition reactions
  - elimination reactions
  - oxidation reactions
  - reduction reactions
  - rearrangements

  Which of these categories would you expect to contain primarily enthalpy-favoured reactions?

  Which of these categories would you expect to contain primarily entropy-favoured reactions?