

Chapter 5. Reactions of Alkenes and Alkynes

Learning objectives:

1. Differentiate primary, secondary, and tertiary carbocations, and recognize the order of stability for these carbocations.
2. Identify the followings from a potential energy diagram when applicable: endothermic or exothermic reactions, activation energy, heat of reaction, locations of transition states, locations of intermediates, and rate-limiting step.
3. Write the electron-pushing (arrow-pushing) mechanisms for hydrohalogenation and hydration.
4. Draw the potential energy diagrams and provide all the applicable information in hydrohalogenation and hydration.
5. Explain the regio- and stereoselectivity issues involving in hydrohalogenation and hydration of alkenes.

Sections to be covered (in the order of delivery):

- 5.1 The addition of a hydrogen halide to an alkene
- 5.2 Carbocation stability depends on the number of alkyl substituents attached to the positively charged carbon
- 5.3 Electrophilic addition reactions are regioselective
- 5.4 The addition of water to an alkene
- 5.5 The addition of an alcohol to an alkene
- 5.6 An introduction to alkynes
- 5.7 The nomenclature of alkynes
- 5.8 The structure of alkynes
- 5.9 The physical properties of unsaturated hydrocarbons
- 5.10 The addition of a hydrogen halide to an alkyne
- 5.11 The addition of water to an alkyne
- 5.12 The addition of hydrogen to alkenes and alkynes
- 5.13 A hydrogen bonded to an sp carbon is acidic
- 5.14 Synthesis using acetylide ions[#]
- 5.15 An introduction to multistep synthesis[#]
- 5.16 Synthetic polymers[#]
- 5.17 Radical in biological systems

[#] Sections that will be skipped

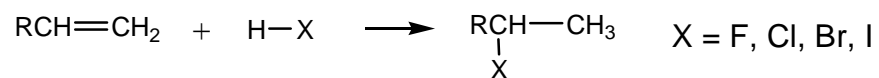
Recommended additional problems

33, 35, 36, 37, 40, 44, 45, 52, 59, 64, 65

5.1 The addition of a hydrogen halide to an alkene (hydrohalogenation)

Know electrophilic addition reaction.

A. General Reaction:



R: alkyl group (example: CH₃-, CH₃CH₂CH₂-)

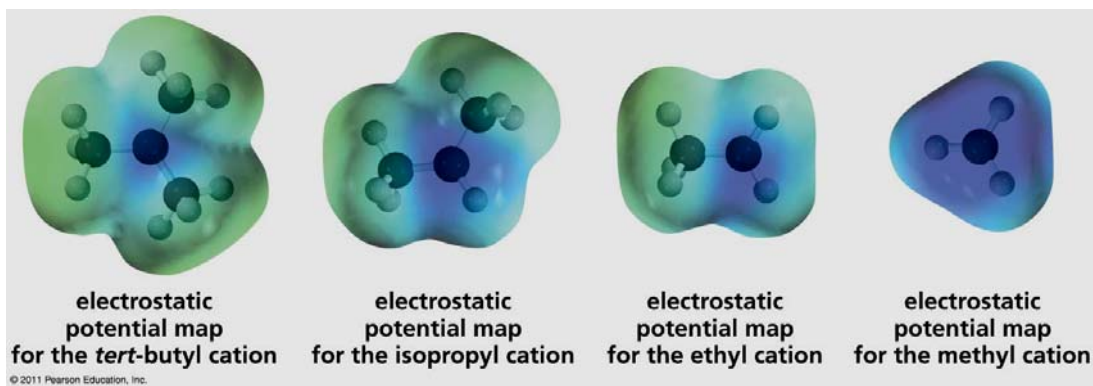
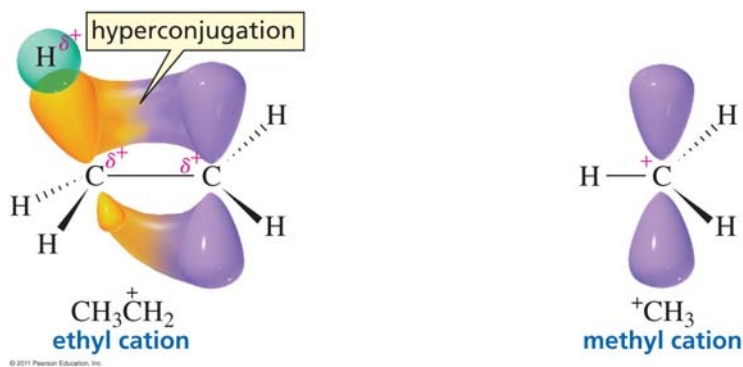
B. Electron-pushing Mechanism:

C. Two possible products can be formed

D. Reaction Energy Diagram

5.2 Carbocation stability depends on the number of alkyl substituents attached to the positively charged carbon

Relative stability of carbocations:



5.3 Electrophilic addition reactions are regioselective

Know what is regioselectivity.

A. Markovnikov's rule:

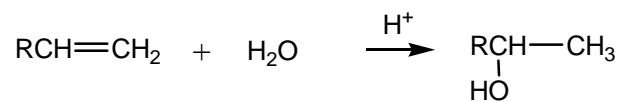
B. Regioselectivity of governed by the stability of carbocation

C. Examples

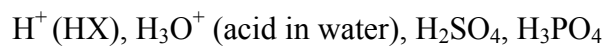
5.4 The addition of water to an alkene (hydration)

A. The addition of water to an alkene is an acid-catalyzed hydration

General Reaction:



Commonly used acid catalysis:



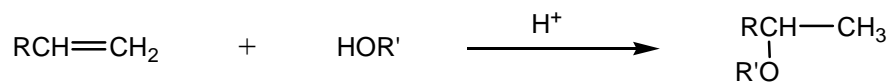
B. Electron-pushing Mechanism:

C. Reaction Energy Diagram

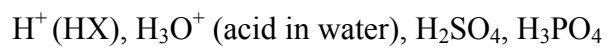
5.5 The addition of an alcohol to an alkene

A. The addition of an alcohol to an alkene is an acid-catalyzed reaction

General Reaction:



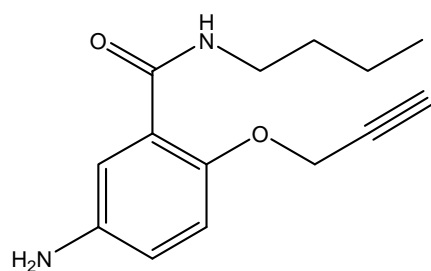
Commonly used acid catalysis (same as hydration):



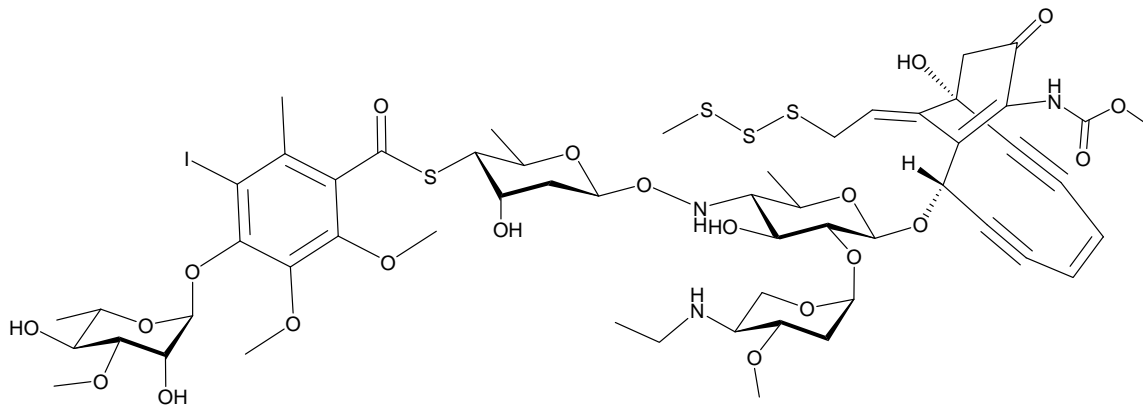
B. Electron-pushing Mechanism:

C. Reaction Energy Diagram

5.6 An introduction to alkynes

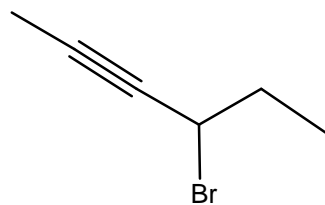
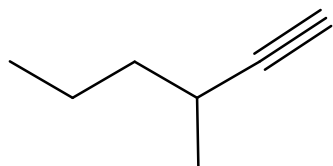
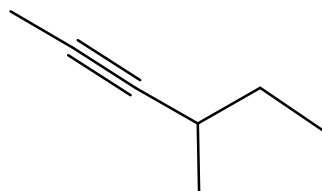
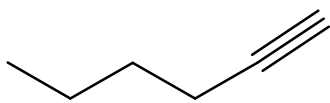


Parsalimide (analgesic)

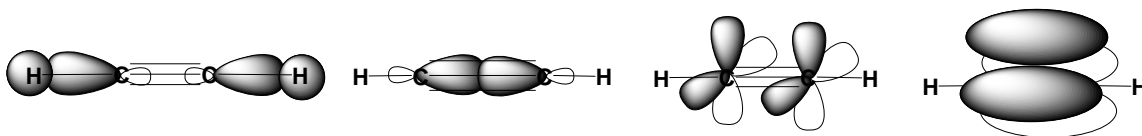
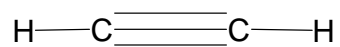


Calicheamicin γ 1 (anticancer)

5.7 The nomenclature of alkynes

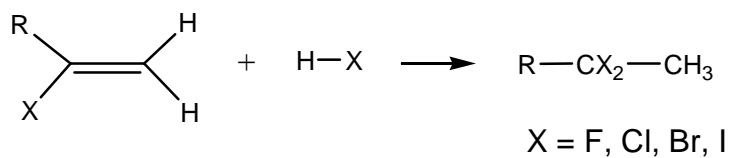
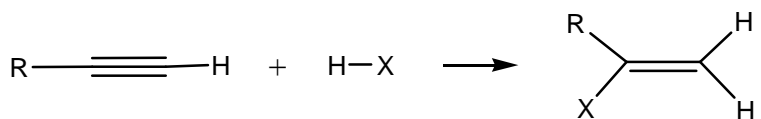


5.8 The structure of alkynes



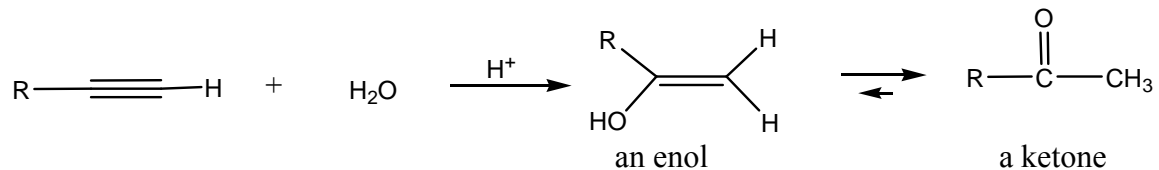
5.9 The physical properties of unsaturated hydrocarbons

5.10 The addition of a hydrogen halide to an alkyne



Electron-pushing Mechanism:

5.11 The addition of water to an alkyne

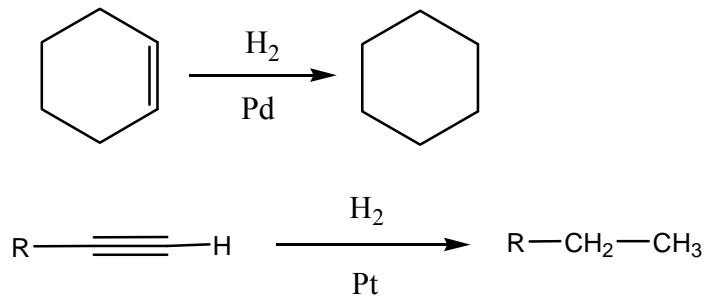


Examples:

5.12 The addition of hydrogen to alkenes and alkynes

A. The addition of hydrogen to alkenes and alkynes is a reduction as known as hydrogenation.

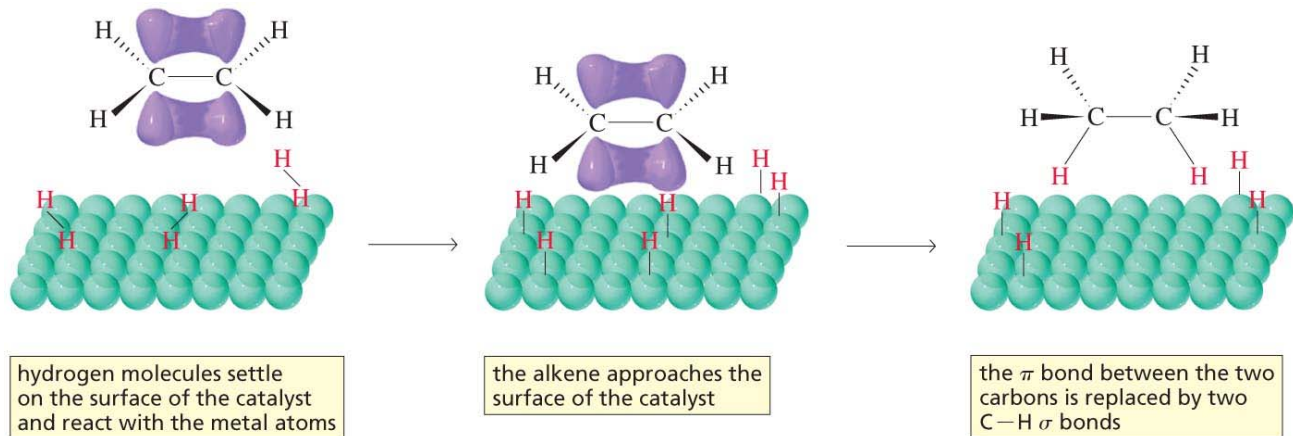
B. Example of catalytic hydrogenation



Variations in Available Metal Catalysts

Pd, Pt [Pt(0), Pt(II)], Ni (Raney Nickel), Rh

C. Syn addition

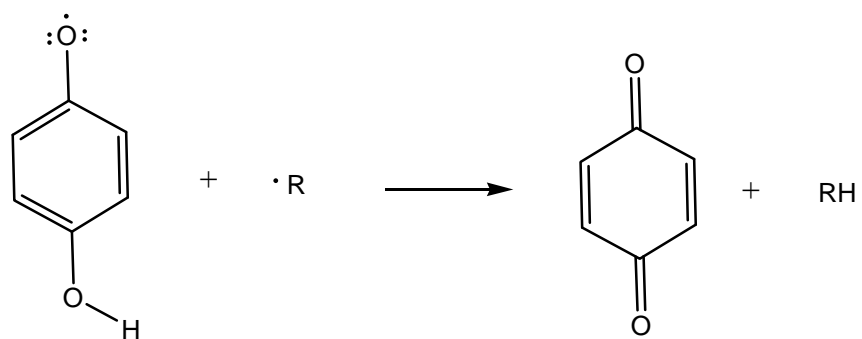
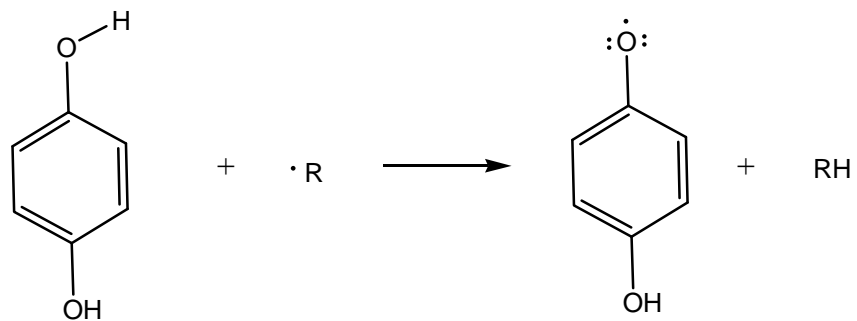


Examples:

5.13 A hydrogen bonded to an sp carbon is acidic

5.17 Radical in biological systems

A. Radical inhibitors



B. Antioxidants

Vitamin C and Vitamin E

