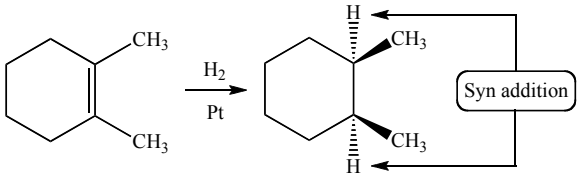
Addition Reactions of Carbon-Carbon Pi Bonds: Miscellaneous Reactions

- Many more addition reactions for pi bonds than we have explored so far!
- Not all are electrophilic addition

Catalytic Hydrogenation

Example:

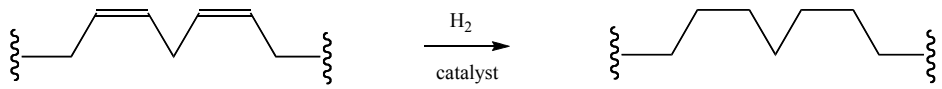


- Thermodynamics: H–H + C–C pi weaker than 2 x C–H so $\Delta G < 0$ and $K_{eq} > 1$
- Kinetics: very slow
- Catalyst: accelerates reaction by $\downarrow E_{act}$ and/or altering reaction mechanism

  Pt, Pd, Ni most common hydrogenation catalysts

- Overall reaction stereochemistry: syn addition
  New C–H bonds formed on same face of alkene
- Overall reaction regiochemistry: not Markovnikov or anti-Markovnikov
- Electrophile: none

Hydrogenated fat:



Unsaturated fat (has C=C)

- Susceptible to oxidation by O_2
- Lower melting point (oil)
- Vegetable oil

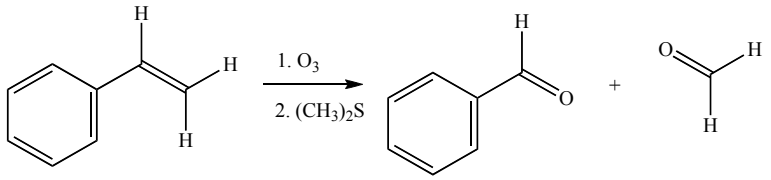
Saturated fat (no C=C)

- Not susceptible to oxidation
- Higher melting point (fat)
- Margarine

Problem: Partial hydrogenation of unsaturated fat converts some *cis*-fat into unhealthful *trans*-fat

Ozonolysis ("ozone breaking")

Example:



- Overall reaction stereochemistry: none
- Overall reaction regiochemistry: not Markovnikov or anti-Markovnikov
- Electrophile: None

What do I need to know about these miscellaneous reactions?

- Reaction products including:

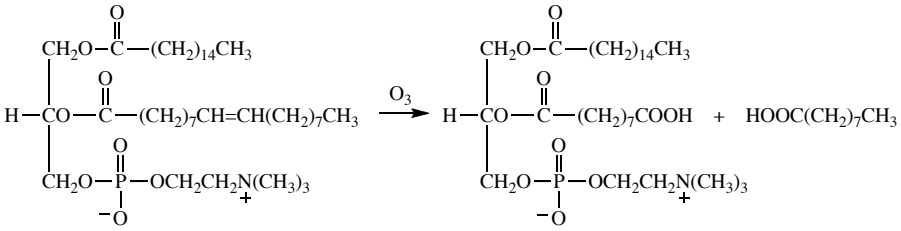
  → stereochemistry (syn, anti, or mixture)

  → regiochemistry (Markovnikov, anti-Markovnikov, mixture, or none of these)
- You are not responsible for the mechanisms

  → Exploring mechanism makes learning stereochemistry & regiochemistry easier

Biological Examples

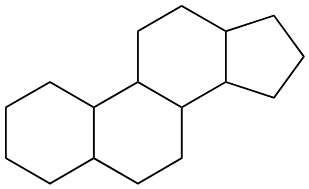
Degradation of Pulmonary Surfactant by Ozone



Surfactant = surface active agent

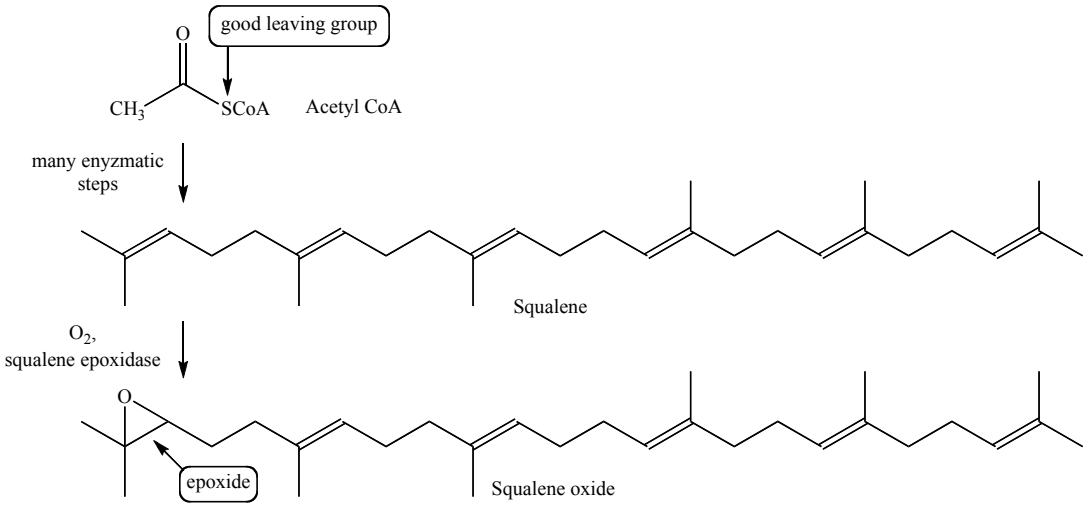
- Requires both polar and nonpolar regions
- Pulmonary surfactant assists migration of O_2 from air to bloodstream
- ↓ nonpolar portion = ↓ surfactant effect = less efficient O_2 migration

Biosynthesis of Steroids

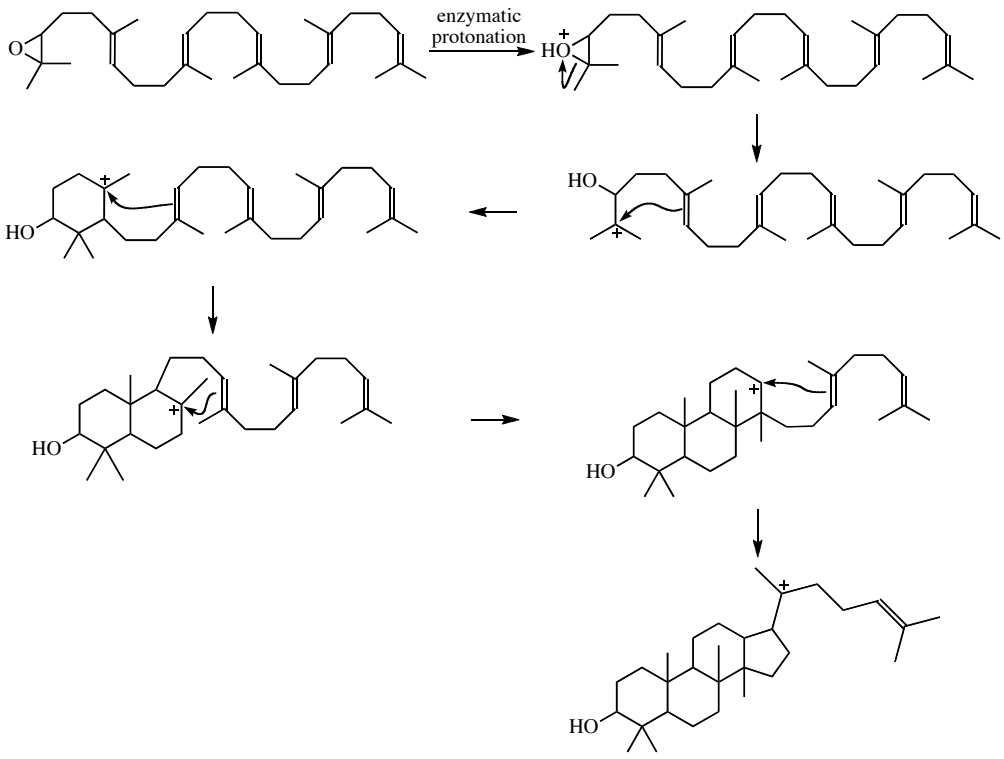


Steroid skeleton

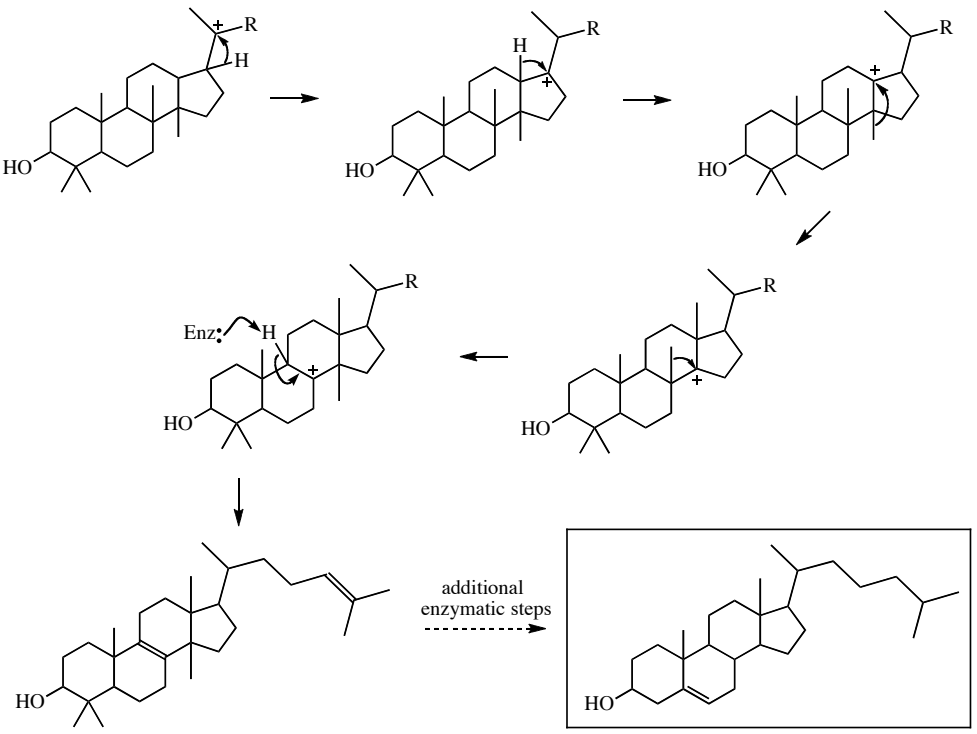
Biosynthetic pathway: start by gathering the carbons....



Form the rings...



Finish up with carbocation fates.....



Lanosterol Cholesterol