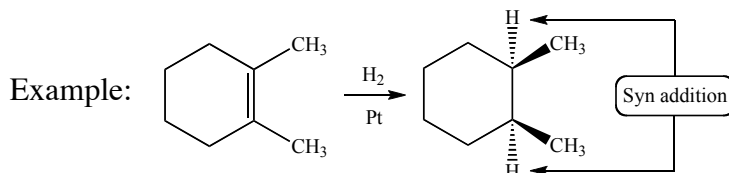


## Addition Reactions of Carbon-Carbon Pi Bonds: Miscellaneous Reactions

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

### Catalytic Hydrogenation

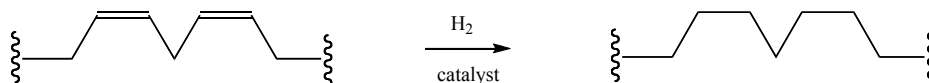


- Thermodynamics:  $\text{H-H} + \text{C-C pi}$  weaker than  $2 \times \text{C-H}$  so  $\Delta G < 0$
- Kinetics: very slow
- Catalyst: accelerates reaction by  $\downarrow E_{\text{act}}$  and/or altering reaction mechanism

Pt, Pd, Ni most common hydrogenation catalysts

- Stereochemistry: syn addition *New C-H bonds formed on same face of alkene*
- Regiochemistry: not Markovnikov or anti-Markovnikov
- Electrophile: none

Hydrogenated fat:



Unsaturated fat (has  $\text{C}=\text{C}$ )

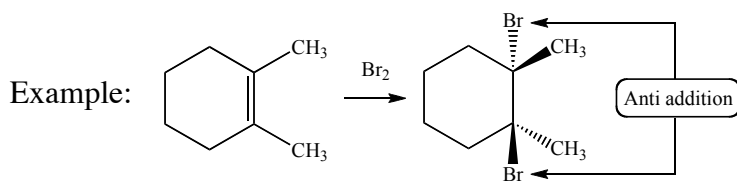
- Susceptible to oxidation by  $\text{O}_2$
- Lower melting point (oil)
- Vegetable oil

Saturated fat (no  $\text{C}=\text{C}$ )

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

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

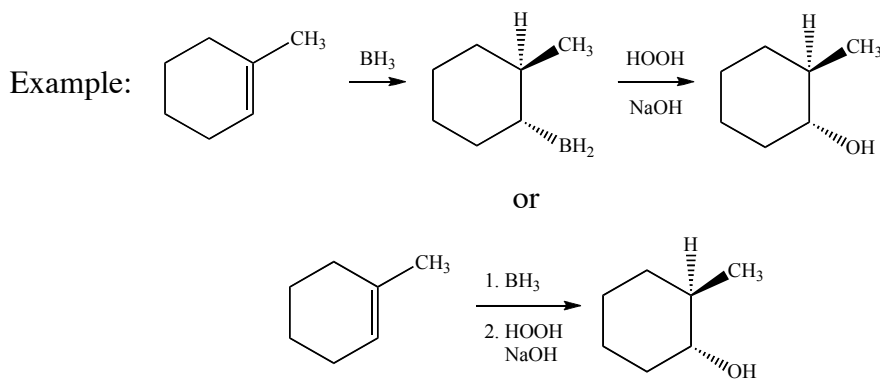
## Addition of Br<sub>2</sub> or Cl<sub>2</sub>



- Stereochemistry: anti addition *New bonds formed on opposite face of alkene*
- Regiochemistry: not Markovnikov or anti-Markovnikov
- Electrophile: Br<sub>2</sub> or Cl<sub>2</sub>

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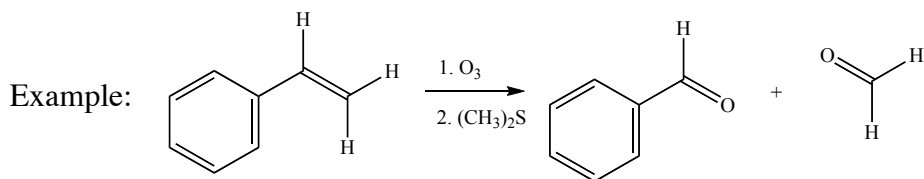
## Hydroboration-Oxidation



- Stereochemistry: syn addition
- Regiochemistry: anti-Markovnikov
- Electrophile: BH<sub>3</sub>

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## Ozonolysis (“ozone breaking”)



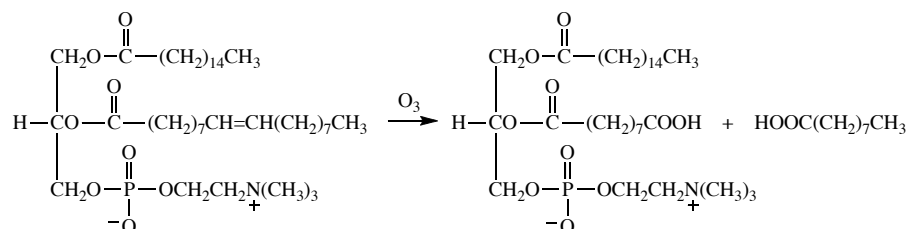
- Stereochemistry: none
- Regiochemistry: not Markovnikov or anti-Markovnikov
- Electrophile: None *Note error in Lecture Supplement*

## 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

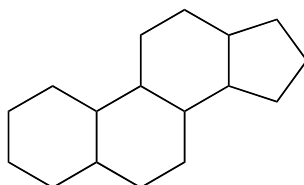


Surfactant = surface active agent

- Requires both polar and nonpolar regions
- Pulmonary surfactant assists migration of O<sub>2</sub> from air to bloodstream
- ↓ nonpolar portion = ↓ surfactant effect = less efficient O<sub>2</sub> migration

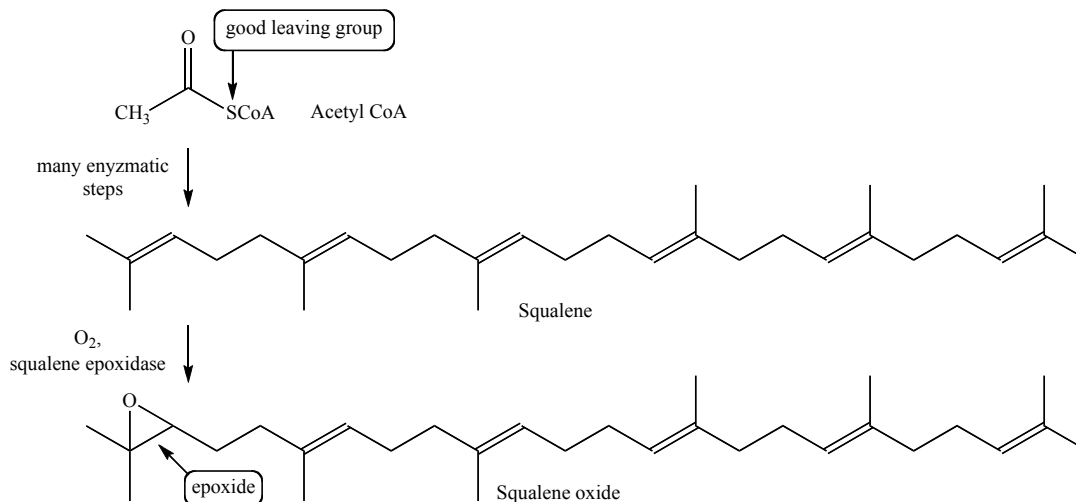
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### Biosynthesis of Steroids

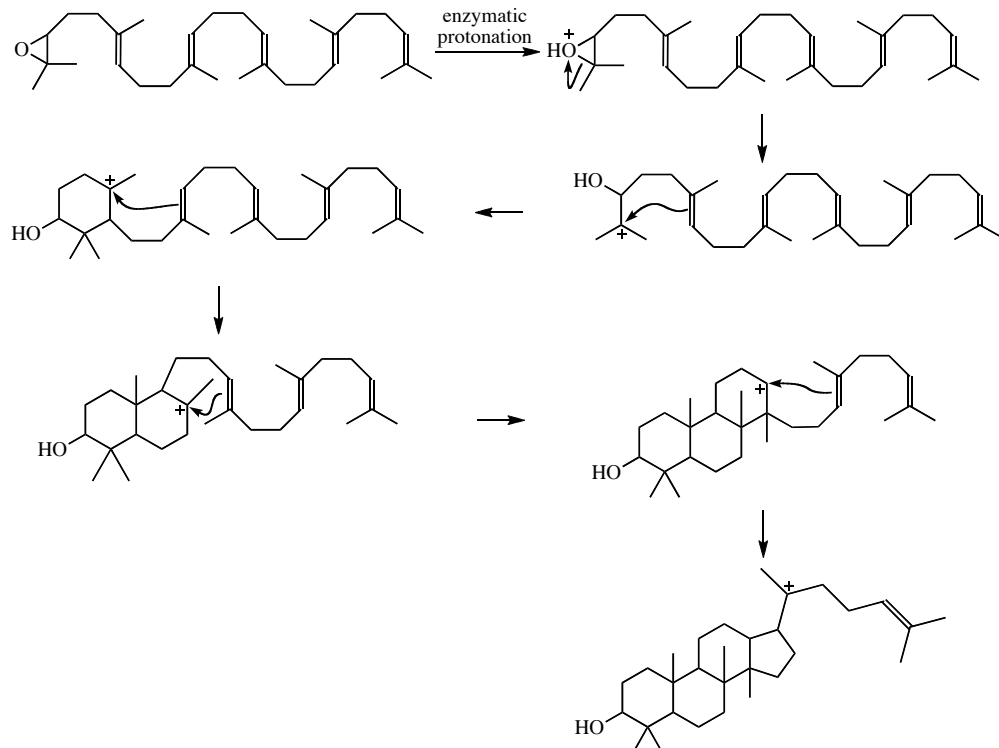


Steroid skeleton

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



Form the rings...



Finish up with carbocation fates....

