Objective 5. Identify a conjugated diene and understand electrophilic addition reactions of dienes.

Skills: Draw structure
ID structural features and reactive sites (alpha C, beta C, LG, etc.)
ID Nu⁻ and E⁺
use curved arrows to show bonds breaking and forming
show delocalized electrons with resonance structures.

Key ideas:
Conjugated dienes are more stable than simple alkenes because of delocalization (draw resonance).
Undergo addition reactions with pi bond as Nu ==> Allylic carbocation forms. Compare to alkene addition.
Apply addition to dienes (1,2 vs. 1,4)
Compounds with More than One C=C bonds are **Polyenes**
Compounds with Two C=C bonds are **Dienes**

**3 Types:**

**Conjugated Dienes:**
2 C=C separated by 1 C-C

**Isolated Dienes:**
2 C=C separated by More Than 1 C-C

**Cumulated Dienes:**
2 adjacent C=C
Fatty Acids: Saturated and Unsaturated
ID the **polyunsaturated** fatty acids. ID diene type.

- **Myristic Acid**
  - coconut oil, butter fat
- **Myristoleic Acid**
  - not common in nature
- **Palmitic Acid**
  - palm and coconut oil
- **Palmitoleic Acid**
  - animal and vegetable oils
  - constituent of glycerides of adipose tissue
- **Oleic Acid**
  - olive oil
  - omega-9 fatty acid
- **Linoleic Acid**
  - safflower oil
  - essential fatty acid
  - omega-6 fatty acid
- **Rumenic Acid**
  - dairy products
Isoprene is a _______ Diene that is used to make polymers: rubber, Gutta-percha

How is rubber different than Gutta-percha? (Hint: zee zame zide)
Which polymer, rubber or Gutta-percha, is more flexible?
**Terpenes** Contain *Isoprene* Units
Found in Essential Oils in Plants

**Types:**
- Hemiterpenes – single isoprene unit (5 carbons)
- Monoterpenes – two isoprene units (10 carbons)
- Sesquiterpenes – three isoprene units (15 carbons)
  and more (diterpenes, sesterterpenes, diterpenes, …)
Chlorophyll is a _________ diene.

http://www.sas.upenn.edu/~patricam/e-portfolio4.htm
More Plant Pigments

**Carotenoids**
(tetraterpenoids)

- Xanthophylls (contain O, e.g., epoxides)
  - e.g., lutein in leafy greens

- Carotenes (no O), e.g., carotene (orange) and lycopene (red)

**Anthocyanins**
– purple and blue

Additional resources:
- [Juicetherapy.co.uk/carrots/](http://www.juicetherapy.co.uk/carrots/)
- [All-free-download.com/free-vector/download/tomato_310440.html](http://all-free-download.com/free-vector/download/tomato_310440.html)
Lutein (Xanthophyll) in leafy greens is a ______ diene.

May help lower risk for cataracts and age-related macular degeneration.
Carotene a _______ diene.

Carotenoids – orange and yellow. May help reduce risk of cancer, heart disease, and age-related macular degeneration.

http://www.sas.upenn.edu/~patricam/e-portfolio4.htm
Are carrots good for your eyes?

- β-carotene
- Vitamin A
- 11-cis-retinal
- Rhodopsin
- cis-trans isomerization
Lab 4. Plant Pigments are Colored
Absorption Spectrum of Chlorophylls and Carotene

http://www.sas.upenn.edu/~patricam/e-portfolio4.htm
Lab 4. Many Plant Pigments are Conjugated
Predict Color of Conjugated Dienes
Use Woodward-Feiser rules to predict color ($\lambda_{\text{max}}$)

<table>
<thead>
<tr>
<th></th>
<th>Wavelength, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conjugated Diene</td>
<td>217</td>
</tr>
<tr>
<td>Each additional double bond extending conjugation</td>
<td>30</td>
</tr>
<tr>
<td>Each auxochromic alkyl group</td>
<td>5</td>
</tr>
<tr>
<td>Each exocyclic double bond</td>
<td>5</td>
</tr>
<tr>
<td>Homoannular diene</td>
<td>39</td>
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</tbody>
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Lab 4. Predict $\lambda_{\text{max}}$ using **Woodward-Feiser Rules**:

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</tr>
</tbody>
</table>

How many: additional double bonds? auxochromic alkyl groups? exocyclic double bonds? homoannular dienes?

**Note**: does **not** work well for compounds that contain more than 6 double bonds in conjugation.
Lab 4. Predict $\lambda_{\text{max}}$ using **Woodward-Feiser Rules**:

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<td>217</td>
<td>217</td>
</tr>
<tr>
<td>Each additional double bond</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>Each auxochromic alkyl group</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Each exocyclic double bond</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Homoannular diene</td>
<td>39</td>
<td>0</td>
</tr>
</tbody>
</table>

How many: additional double bonds?  
auxochromic alkyl groups?  
exocyclic double bonds?  
homoannular dienes?

**Note**: does not work well for compounds that contain more than 6 double bonds in conjugation.

$$\lambda_{\text{max}} = 327 \text{ nm}$$
Lab 4. For polyenes with > 6 pi bonds, use *Feiser-Kuhn Rules*:

\[ \lambda_{\text{max}} = 114 + 5M + n (48.0 - 1.7n) - 16.5 R_{\text{endo}} - 10 R_{\text{exo}} \]

where,

- \( \lambda_{\text{max}} \) = wavelength of maximum absorption
- \( M \) = number of alkyl substituents / ring residues in the conjugated system
- \( n \) = number of conjugated double bonds
- \( R_{\text{endo}} \) = number of rings with endocyclic (inside ring) double bonds in the conjugated system
- \( R_{\text{exo}} \) = number of rings with exocyclic (outside ring) double bonds in the conjugated system.

Lab 4. Is β-Carotene a conjugated diene?
Predict $\lambda_{\text{max}}$ using _____ Rules (observed $\lambda_{\text{max}} = 452$ nm)
Lab 4. Is β-Carotene a conjugated diene? Predict $\lambda_{\text{max}}$ using Feiser-Kuhn Rules (observed $\lambda_{\text{max}} = 452$ nm)

$$\lambda_{\text{max}} = 114 + 5M + n (48.0 - 1.7 n) - 16.5 R_{\text{endo}} - 10 R_{\text{exo}}$$

$$= 114 + 5(10) + 11 (48.0 - 1.7 (11)) - 16.5 (2) - 10 (0)$$

$$= 453.3 \text{ nm (vs. observed } \lambda_{\text{max}} = 452 \text{ nm)}$$
Lab 4. Is Lycopene a conjugated diene?
Predict $\lambda_{\text{max}}$ using _____ Rules (observed $\lambda_{\text{max}} = 474$ nm)

http://www.organic-herb.com/Product/Item/75.html

HPLC Chromatogram of Lycopene
Amethstin (red-violet protozoan pigment) structure solved. C&EN, 6/9/14, p. 29 (http://cen.acs.org/articles/92/i23/Protozoan-Pigment-Puzzle-Solved.html)

Predict $\lambda_{\text{max}}$
Lab 4. Dye Sensitized Solar Cell using Fruit and Vegetables

Are plant pigments conjugated?
Bring colored fruit/vegs to lab.
http://climafluttuante.blogspot.com/2010_10_01_archive.html
Dye-sensitized solar cells
Maximum certified efficiency: 11.9%

Light transmitted by the transparent electrode of a dye-sensitized solar cell is absorbed by a dye (red), which coats TiO$_2$ nanoparticles (gray). The process forms electron-hole pairs (e$^-$/h$^+$). Electrons travel through the TiO$_2$ layer to one electrode as holes travel through an electrolyte (blue) to the other electrode, generating electric current. ([http://cen.acs.org/articles/94/i18/future-low-cost-solar-cells.html](http://cen.acs.org/articles/94/i18/future-low-cost-solar-cells.html))
Are anthocyanins (purple and blue) conjugated dienes?
https://en.wikipedia.org/wiki/Anthocyanin

May help reduce risk of cancer, stroke, and heart disease.
OLED (Organic Light Emitting Diodes): are these compounds conjugated?

Penta(2-thienyl)pyridine

Pentacene

Phthalocyanine

Benzofuran-fused oxophosphole

Polythiophene

[CEN, 1/21/13, p. 27]

http://www.sonyinsider.com/2009/05/21/the-science-of-sonys-attraction-to-flexible-oled/]
Compounds with More than One C=C bonds are **Polyenes**
Compounds with Two C=C bonds are **Dienes**

3 Types:
**Conjugated Dienes:** most stable
2 C=C separated by 1 C-C

**Isolated Dienes:** less stable
2 C=C separated by More Than 1 C-C

**Cumulated Dienes:** least stable.
2 adjacent C=C

Why are **Conjugated** Dienes the **Most Stable**?

Identify hybridization at each C in each diene.
Which diene is most like an alkyne?
Which diene has delocalized $\pi$ electrons?
A Conjugated Diene has Delocalized $\pi$ electrons

\[
\begin{array}{ccc}
\text{C-C length} & 153 \text{ pm} & 151 \text{ pm} & 148 \text{ pm} \\
\text{C=C length} & 134 \text{ pm} & \\
\end{array}
\]

Draw resonance structures for 1,3-butadiene. Are the resonance structures equivalent? If not, which is the major contributor?

Which pi bond is the most reactive? Why?
7-epizingiberene is found in wild tomatoes. It deters whiteflies, spider mites, and aphids eat tomatoes bound and spread viruses that can destroy entire shipments in the $53 billion industry. Genetic engineering - gene to produce 7-epizingiberene introduced into commercial tomatoes in their stems and leaves but not in their fruit.

Pi bonds are _____.

At which pi bond will HCl react? Why?
**Dienes Undergo Addition Reactions**

- **Isolated** Dienes React Like Alkenes
- **Cumulated** Dienes React Like Alkynes (see sp hybridized C)
- **Conjugated** Dienes React Like Alkenes but with a “Twist”

Focus on **Conjugated** Diene Addition Reactions

![Dienes Reaction](image)

Draw all possible products of this reaction. Use curved arrows to show how each product is formed.
Which product is the most likely product? Why?
Dienes Undergo Addition Reactions

Conjugated Dienes React Like Alkenes but with a “Twist”

Addition of HX to Conjugated Diene Produces Two R-X Products: 1, 2 Addition and 1, 4 Addition Products

1, 2 and 1, 4 refers to relative position of H and X in products

Use Curved Arrows to show how products are formed.
Addition of HX to Conjugated Diene Forms an **Allylic** Carbocation Intermediate

Which C⁺ intermediate is more stable?

Which product is more stable?
Addition of HX to Conjugated Diene forms **Allylic Halide**

Two ways to synthesize 1-bromo-2-butene.

Which method is better?
Predict the product(s) of each reaction:

a. \[ \text{HBr} \]

b. \[ \text{HBr} \]

See Practice Problems
One diene produces 4 products whereas the other diene produces 2. Explain.

See Practice Problems
Klein, Problem 17.35. Identify the structure of the conjugated diene that will react with one equivalent of HBr to yield a racemic mixture of 3-bromocyclohexene.

See Practice Problems
Conjugated Polyenes undergo Addition

Conjugated diene $\rightarrow$ 1,2 product and 1,4 product

Conjugate triene $\rightarrow$ 1,2 product and 1,4 product and ??

Conjugate tetraene $\rightarrow$ 1,2 product and 1,4 product and ??
Lab 4: Conjugated Polyenes are found in Plant Pigments

Does Carotene undergo addition?

How many pi bonds are conjugated?
How many possible products?
Zeaxanthin (very common carotenoid alcohol found in nature) is a _____ diene.

Reaction conditions?

Violaxanthin (type of Xanthophyll) is a ______ diene.
Orange pigment found in many plants, e.g., pansies.

http://www.sas.upenn.edu/~patricam/e-portfolio4.htm
**Objective:** How are dienes prepared?

Dienes are Prepared from an Alkene with a Leaving Group
The LG is Involved in an **Elimination** Reaction
Where should the LG be relative to the $\pi$ bond to make a conjugated diene?

The more stable product is formed. Which product is more stable?
**Objective**: Predict the product of each reaction
cyclohexene reacted with $\text{Br}_2 / \text{CH}_2\text{Cl}_2$ then with $\text{KOH} / \text{heat}$

What does pi bond do?  
Is $\text{Br}_2$ a Nu:− or E+?

What does KOH do?
**Objective:** Predict the product of each reaction

1-butene reacted with N-bromosuccinimide (NBS) then treated with KOH/ heat

\[ \text{allylic position} \]

ID structural features

What does KOH do?

1,3-butadiene + HBr -->

\[ \text{HBr} \]
1,2 product vs. 1,4 product

Reaction Temperature Determines Product Distribution

\[
\text{HBr} \quad \text{Br}^+ \quad + \quad \text{Br}^- \\
\text{T} = 0^\circ C \quad 71\% \quad 29\%
\]

\[
\text{T} = 40^\circ C \quad 15\% \quad 85\%
\]

Structural feature of products: allylic bromide
Reaction Temperature Determines Product Distribution

Low T (0°C) ==> More stable intermediate (Kinetic Control) ==> Less stable product

High T (40°C) ==> Less stable intermediate ==> More stable product (Thermodynamic Control)
**Objective**: Predict the product or ID the reaction conditions

\[
\text{isoprene} + \text{HBr} \xrightarrow{40^\circ \text{C}} \text{allylic bromide}
\]

Structural feature of products:

- More stable
- Less stable

T = high or low?
**Objective**: Predict the product or ID the reaction conditions

\[ ? + \text{HBr} \xrightarrow{T^0?C} \]

Identify structural features of product: **allylic bromide**

Does **allylic bromide** come from 1,2 or 1,4 addition of conjugated diene?

Is reactant A or B?

[Diagram of reactants A and B with chemical structures]
**Objective**: Predict the product or ID the reaction conditions

? + HBr $\xrightarrow{T^\circ?C}$

Does **allylic bromide** come from 1,2 or 1,4 addition of conjugated diene?
Is reactant A or B?

Predict products at high and low T
Lavendar oil – fragrance, antiseptic, and antioxidant contains linalool (terpene)

http://cen.acs.org/articles/92/i41/Problem-Lavender-Oil.html

What starting material would you use to make linalool?
Addition of $X_2$ to Conjugated Diene Tends to Form 1, 4 Addition Product
Add Allylic and Diene Reactions to your Organic Reaction Map
**Diels-Alder Reaction: Make a Ring from a Chain**
Conjugated Diene + Dienophile --> Ring

Electron Withdrawing Groups (EWG): NO₂, CN, COOH, CHO

*What makes a group an EWG?*

Reaction occurs in **ONE** step: no reaction intermediates detected ==> **Pericylic** Mechanism
Two conformations for conjugated dienes:

s-cis

s-trans

s refers to rotation about a sigma (σ) bond

Need s-cis for Diels-Alder reaction

Which conformer is more stable?  s-cis    s-trans
Diels-Alder involved in Cortisone synthesis (LearnBacon.com)
Cortisone used to treat inflammation but side effects include hyperglycemia, anxiety/depression, glaucoma, and osteoporosis.

dienophile + diene → Diels-Alder Product

Cortisol is an adrenal gland hormone for the treatment of inflammation.
Diels-Alder used to make prostaglandin F2-alpha – used to induce labor in pregnant women. (LearnBacon.com)

What is the structure of the bicyclic product?
Diels-Alder used to make prostaglandin F2-alpha – used to induce labor in pregnant women. (LearnBacon.com)

What is the structure of the bicyclic product?
Intramolecular Diels-Alder reactions: synthesis of Lovastatin (cholesterol lowering drug) and biosynthesis of solanapyrone A (DNA polymerase inhibitor). (LearnBacon.com)
Vitamin D biosynthesis involves a Pericyclic Reaction (Klein, p. 800)

Ergosterol

vegetables

7-dehydrocholesterol

fish and dairy

Vitamin D:
Vitamin $D_3$ = cholecalciferol
Vitamin $D_2$ = ergocalciferol
If you like *Allylic* Compounds, Try these:

1. Show how to prepare the following compound from propene and any necessary organic or inorganic reagents: allyl alcohol

\[
\ce{\text{CH}_2=\text{CHCH}_2\text{OH}}
\]

2. Suggest a reasonable explanation for the following observation:
After a solution of 3-buten-2-ol in aqueous sulfuric acid had been allowed to stand for 1 week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol.
**Problem solving steps:**
1. Identify functional group(s)
2. Relate reaction conditions to reaction type

Determine the product of each reaction:

```
\[
\text{C}_6\text{H}_5
\]

1. \(\text{B}_2\text{H}_6\)
2. \(\text{H}_2\text{O}_2, \text{OH}^-\)

```

```
\[
\text{OH}
\]

1. \(\text{H}_2\text{SO}_4\)

```
FG = alkene
Conditions: addition to make alcohol, non-Markovnikov

FG = alcohol
Conditions: elimination to make alkene
**Problem solving steps:** 1. Identify functional group(s)  
2. Relate reaction conditions to reaction type

α-Terpinene is a pleasant smelling compound present in the essential oil of marjoram. α-Terpinene undergoes hydrogenation with 2 equiv of H₂ to produce 1-isopropyl-4-methylcyclohexane. Ozonolysis of α-Terpinene yields the following two compounds:

![Structure of α-Terpinene](image)

What is the structure of α-Terpinene? (Klein, Problem 17.60)
What is the structure of $\alpha$-Terpinene?

$$\text{FG} = \text{ketone/aldehyde}$$

$\text{Conditions:}$ alkene bond cleavage