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:

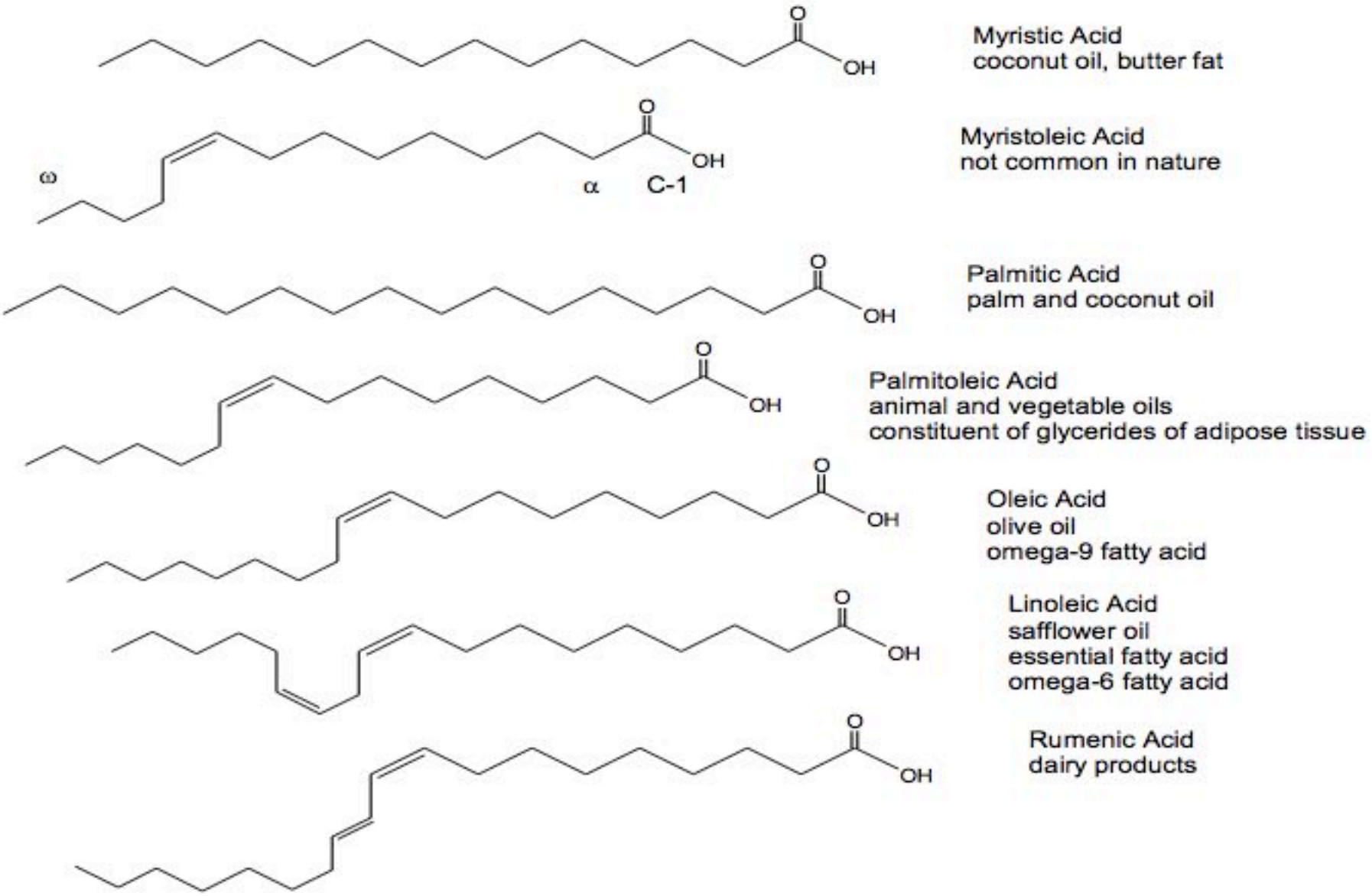
Conjugated Dienes:
2 C=C separated by 1 C-C

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

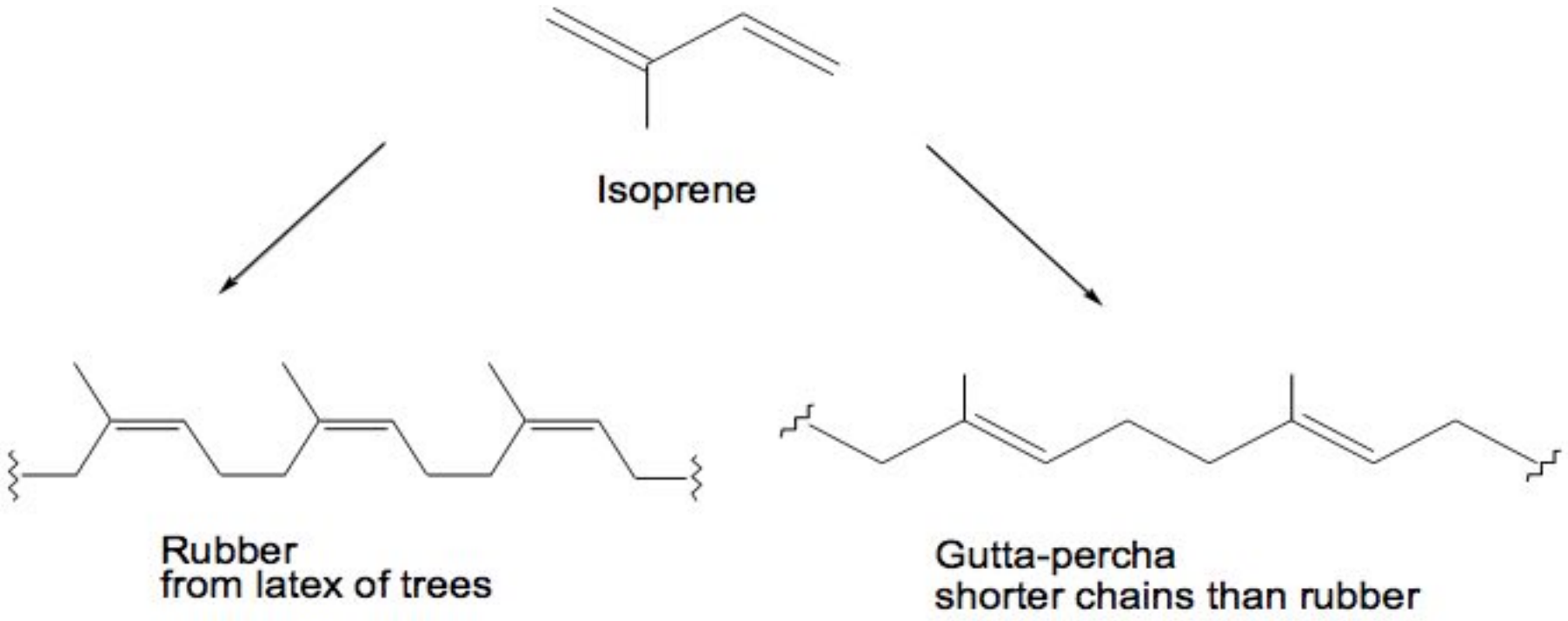
Cumulated Dienes:
2 adjacent C=C

Fatty Acids: Saturated and Unsaturated

ID the polyunsaturated fatty acids. ID diene type.



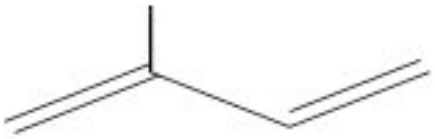
Isoprene is a _____ Diene that is used to make polymers: rubber, Gutta-percha



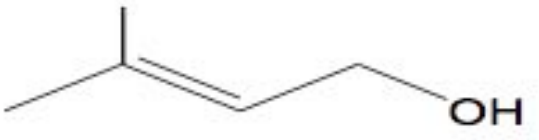
How is rubber different than Gutta-percha? (Hint: zee zame zide)
Which polymer, rubber or Gutta-percha, is more flexible?

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, …)

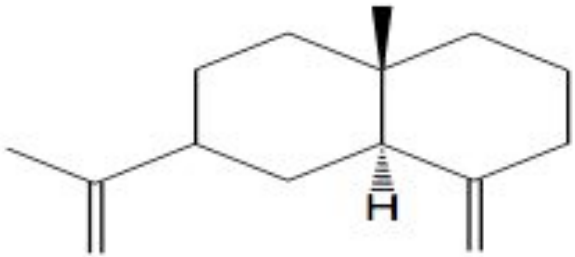


Isoprene



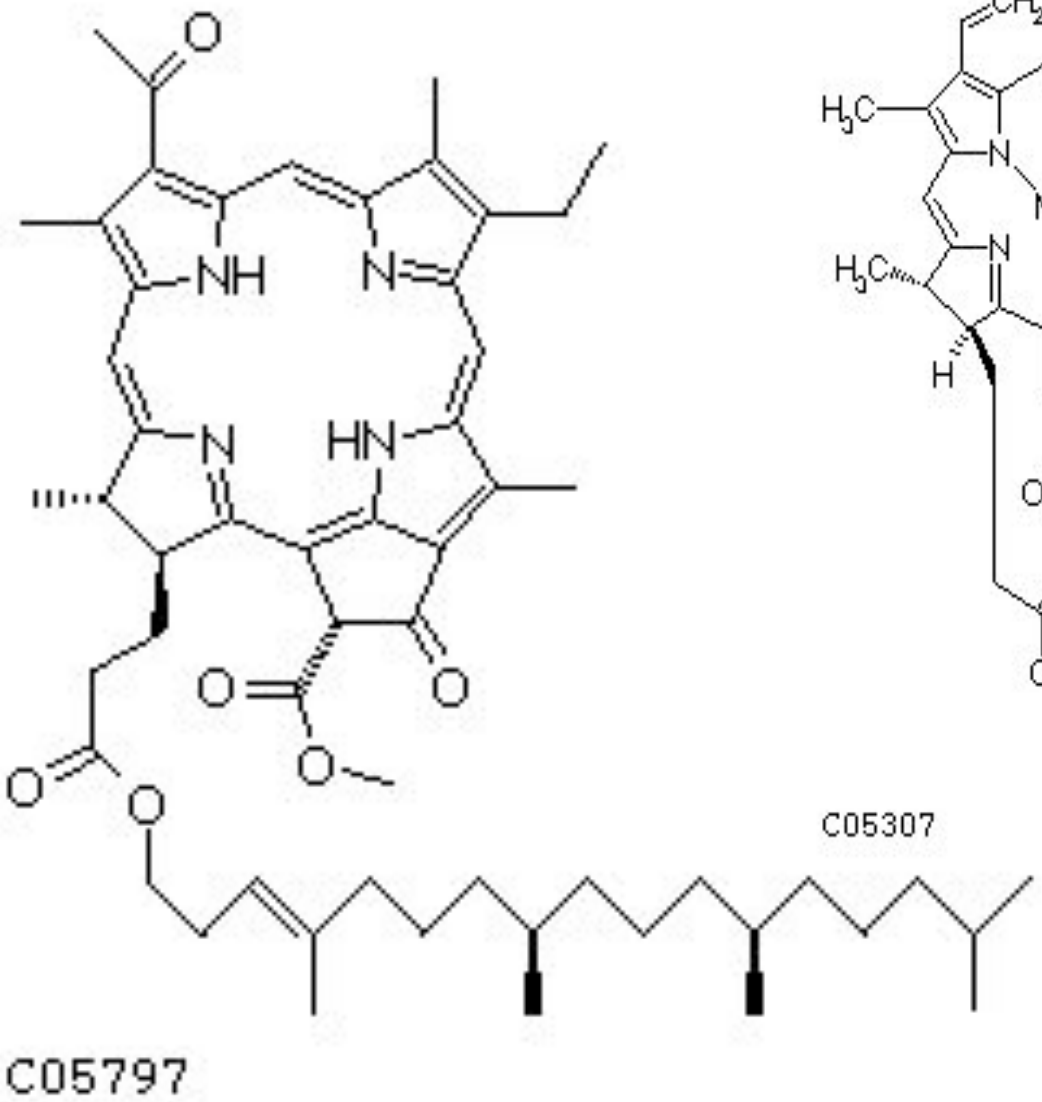
Prenol - citrus fruits

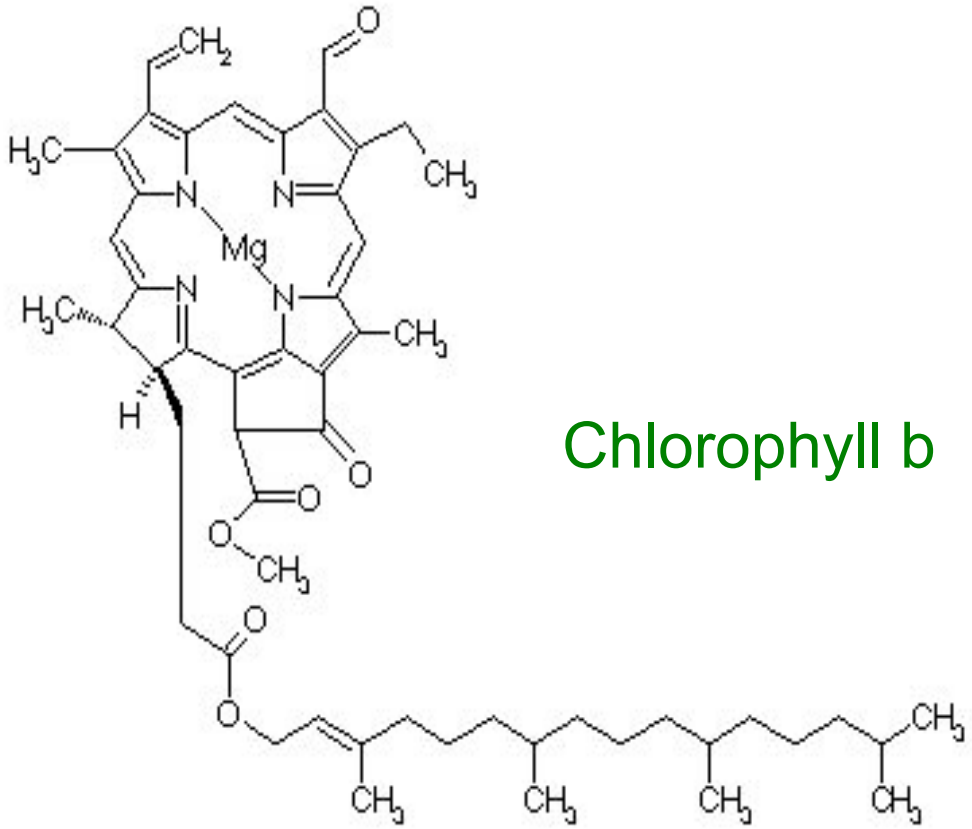
Citral - lemon grass



α -Selinene - celery

Chlorophyll is a _____ diene.





Chlorophyll b

Chlorophyll a

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

More Plant Pigments

Carotenoids
(tetraterpenoids)

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

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

http://keworganics.com.au/product/spinach-organic-bunch/

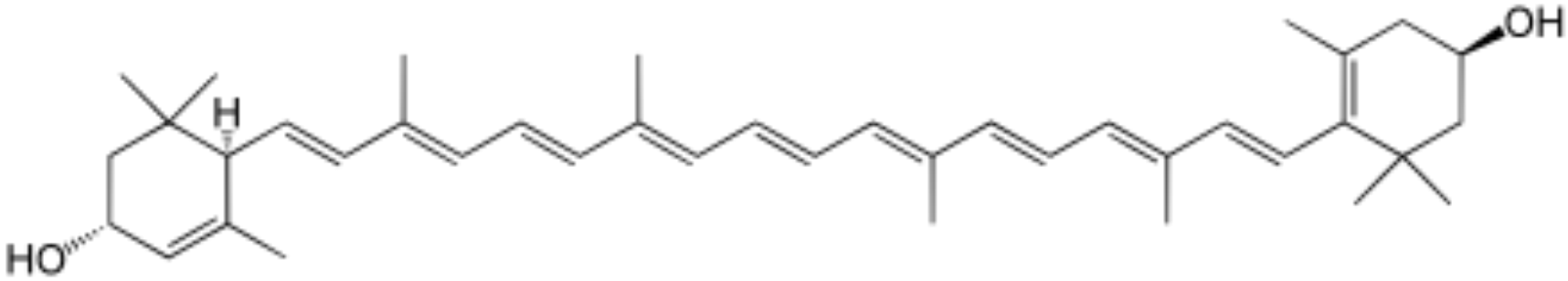
http://all-free-download.com/free-vector/download/tomato_310440.html

http://www.juicetherapy.co.uk/carrots/

Anthrocyanins
– purple and blue

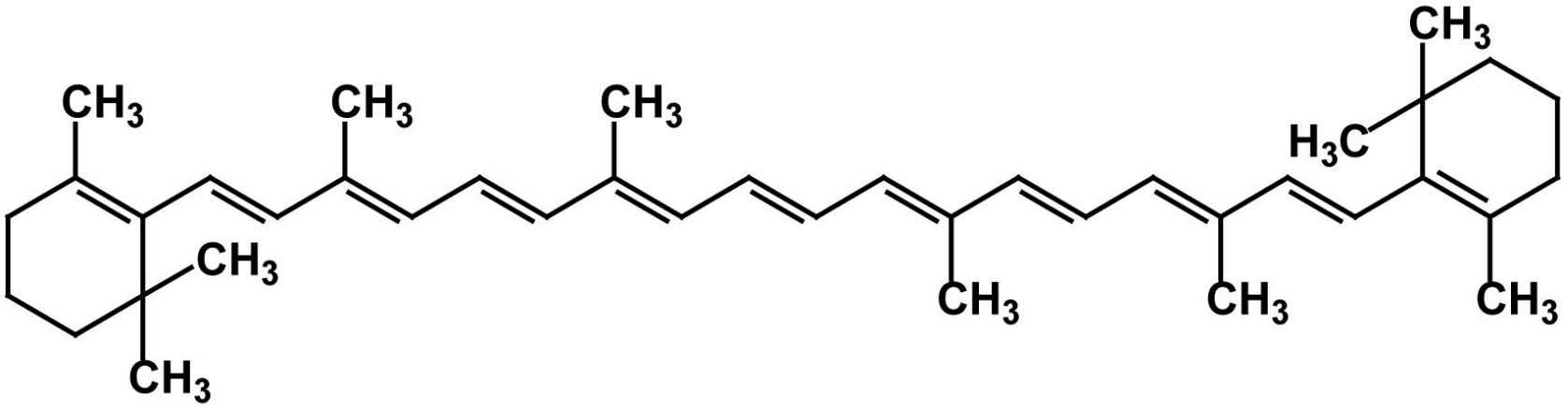
http://authoritynutrition.com/10-proven-benefits-of-blueberries/

Lutein (Xanthophyll) in leafy greens is a _____ diene.



May help lower risk for cataracts and age-related macular degeneration.

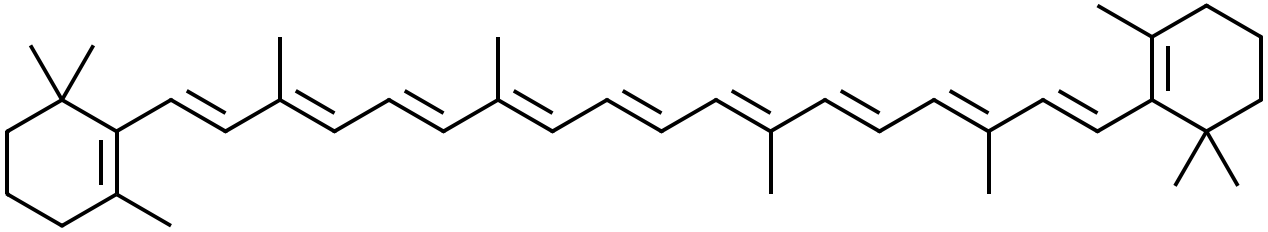
Carotene a _____ diene.



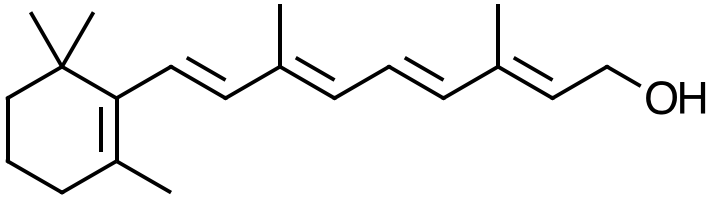
Carotenoids – orange and yellow. May help reduce risk of cancer, heart disease, and age-related macular degeneration.

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

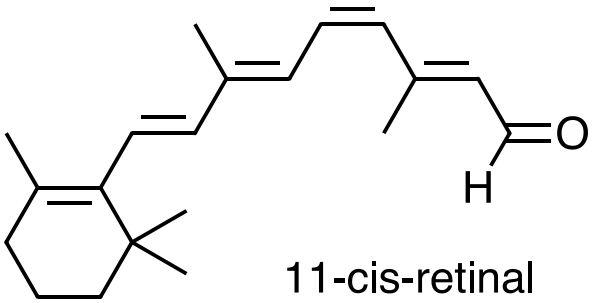
Are carrots good for your eyes?



β-carotene

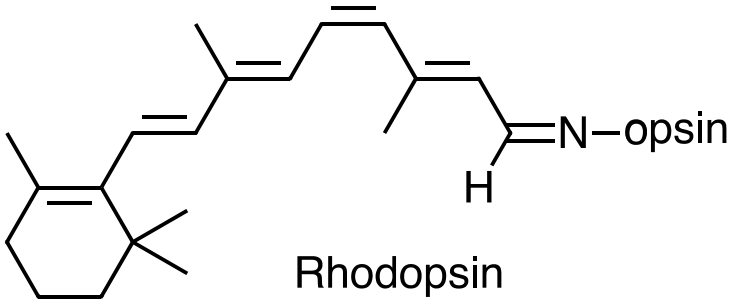


Vitamin A



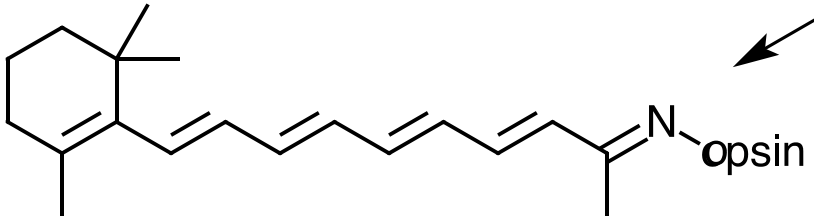
11-cis-retinal

H_2N-opsin



Rhodopsin

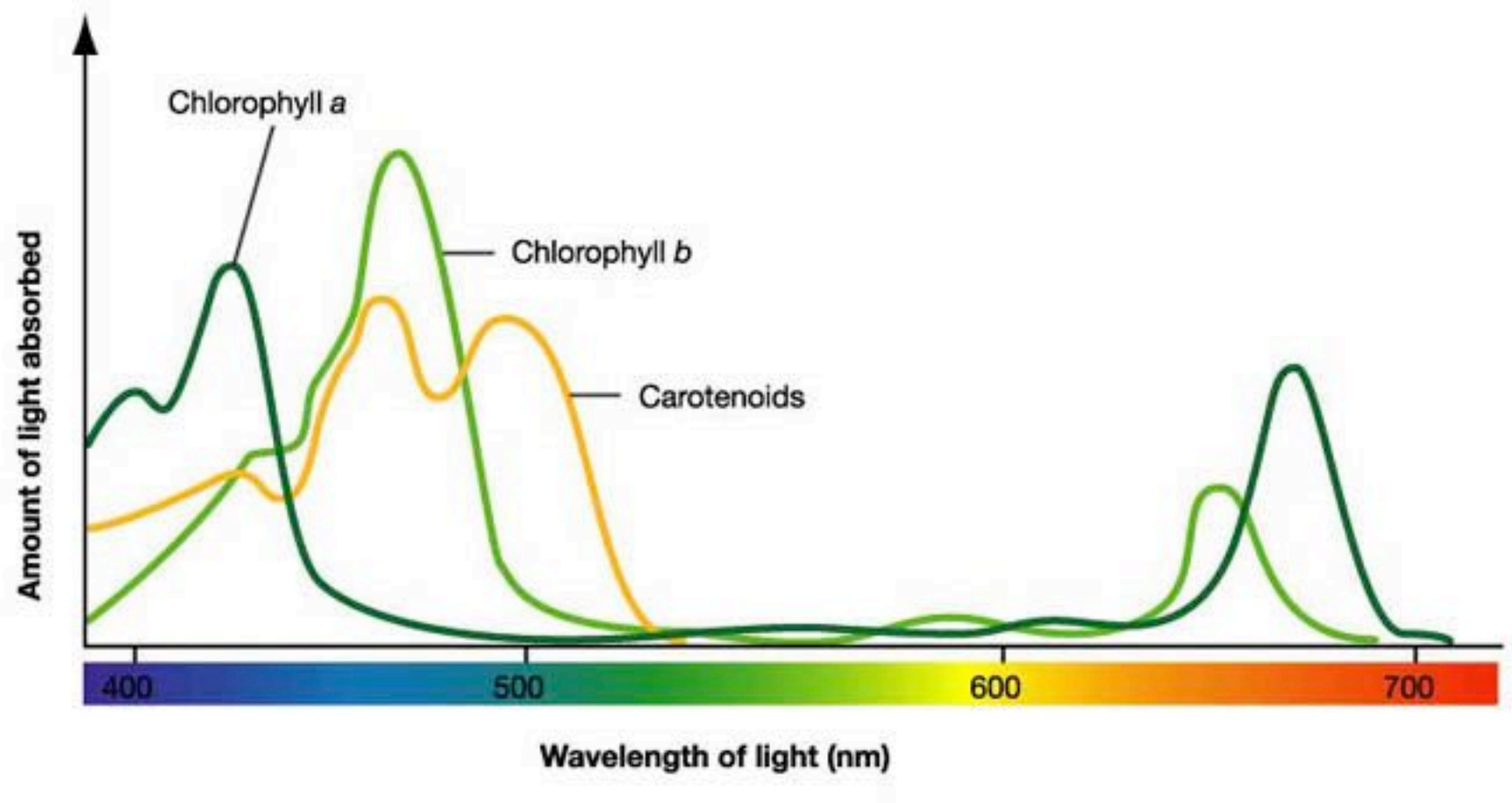
hv



cis-trans
isomerization

Lab 4. Plant Pigments are Colored

Absorption Spectrum of Chlorophylls and Carotene



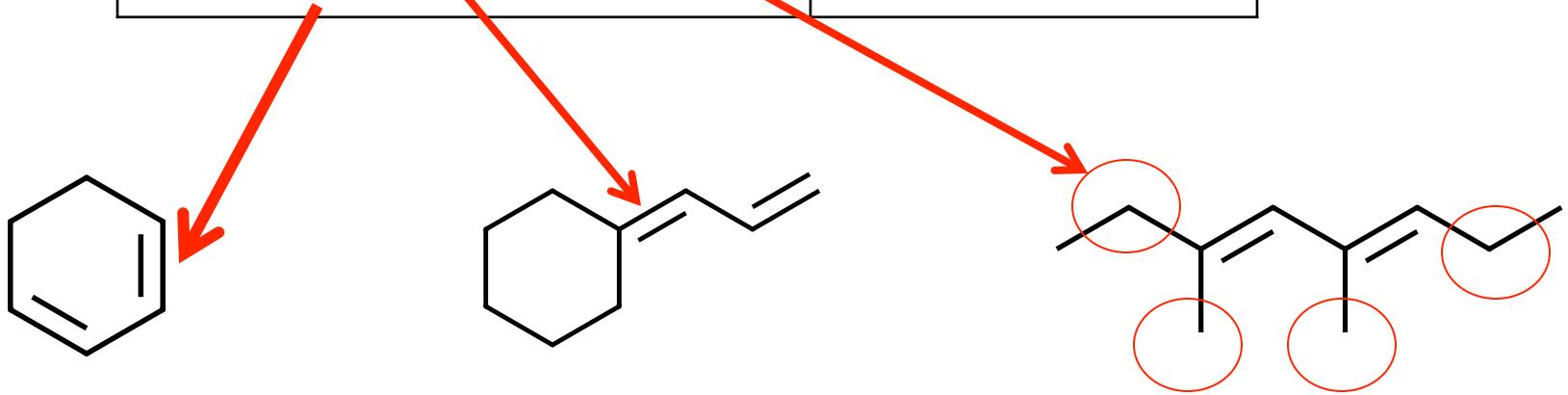
http://www.sas.upenn.edu/~patricam/e-portfolio4.htm

Lab 4. Many Plant Pigments are Conjugated

Predict Color of Conjugated Dienes

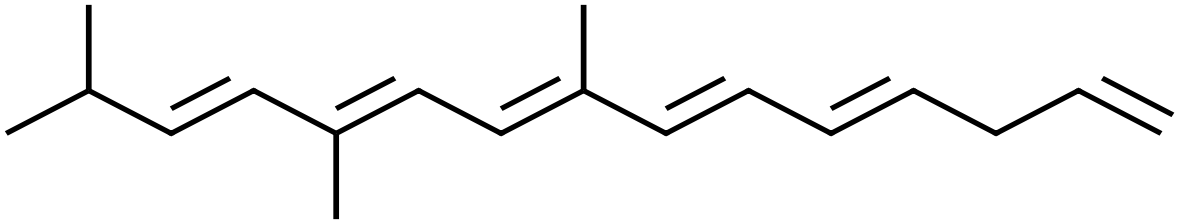
Use ***Woodward-Feiser*** rules to predict color (λ_{max})

	Wavelength, nm
Conjugated Diene	217
Each additional double bond extending conjugation	30
Each auxochromic alkyl group	5
Each exocyclic double bond	5
Homoannular diene	39



Lab 4. Predict λ_{max} using ***Woodward-Feiser Rules***:

	Wavelength, nm
Conjugated Diene	217
Each additional double bond	30
Each auxochromic alkyl group	5
Each exocyclic double bond	5
Homoannular diene	39



How many: additional double bonds?

auxochromic alkyl groups?

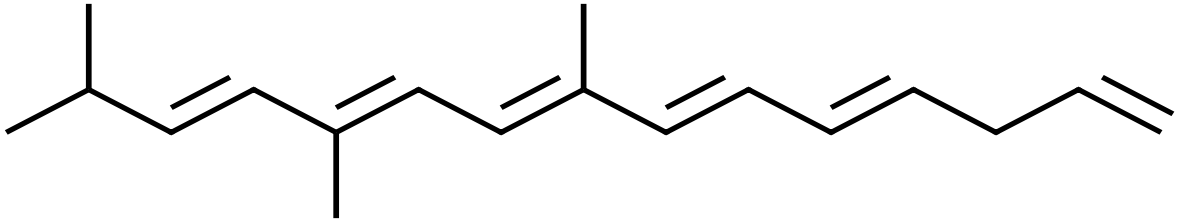
exocyclic double bonds?

homoannular dienes?

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

Lab 4. Predict λ_{max} using ***Woodward-Feiser Rules***:

	Wavelength, nm	#	
Conjugated Diene	217		217
Each additional double bond	30	3	90
Each auxochromic alkyl group	5	4	20
Each exocyclic double bond	5	0	0
Homoannular diene	39	0	0



How many: additional double bonds?

auxochromic alkyl groups?

exocyclic double bonds?

homoannular dienes?

λ_{max} = 327 nm

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

Lab 4. For polyenes with > 6 pi bonds, use ***Feiser-Kuhn Rules***:

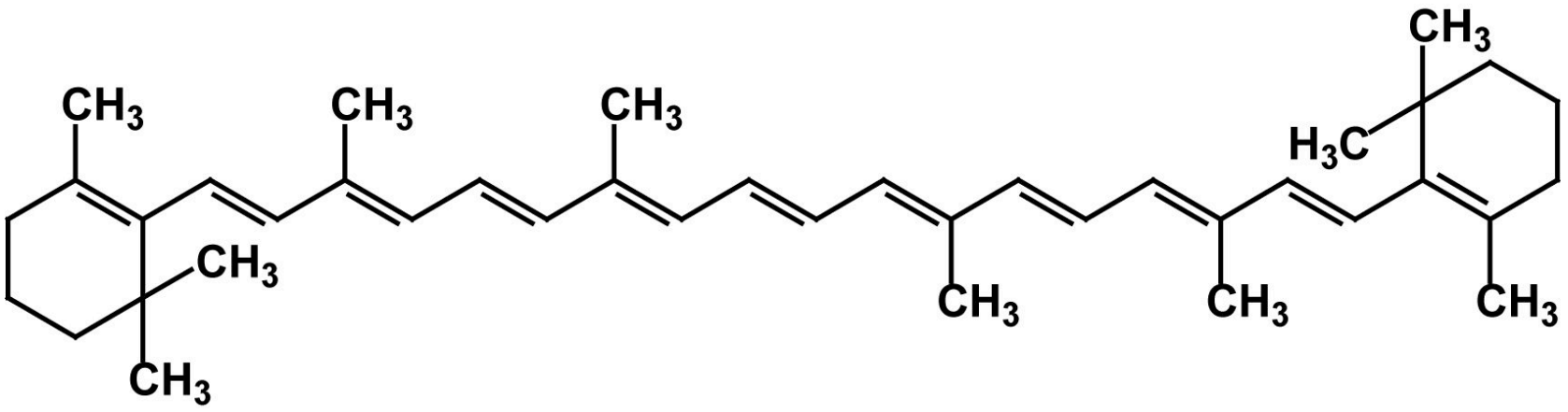
$\lambda_{max} = 114 + 5M + n\,(48.0 - 1.7\,n) - 16.5\,R_{endo} - 10\,R_{exo}$

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

http://pharmaxchange.info/press/2013/05/ultraviolet-visible-uv-vis-spectroscopy-%E2%80%93-fieser-kuhn-rules-to-calculate-wavelength-of-maximum-absorption-lambda-max-of-polyenes-with-sample-problems/

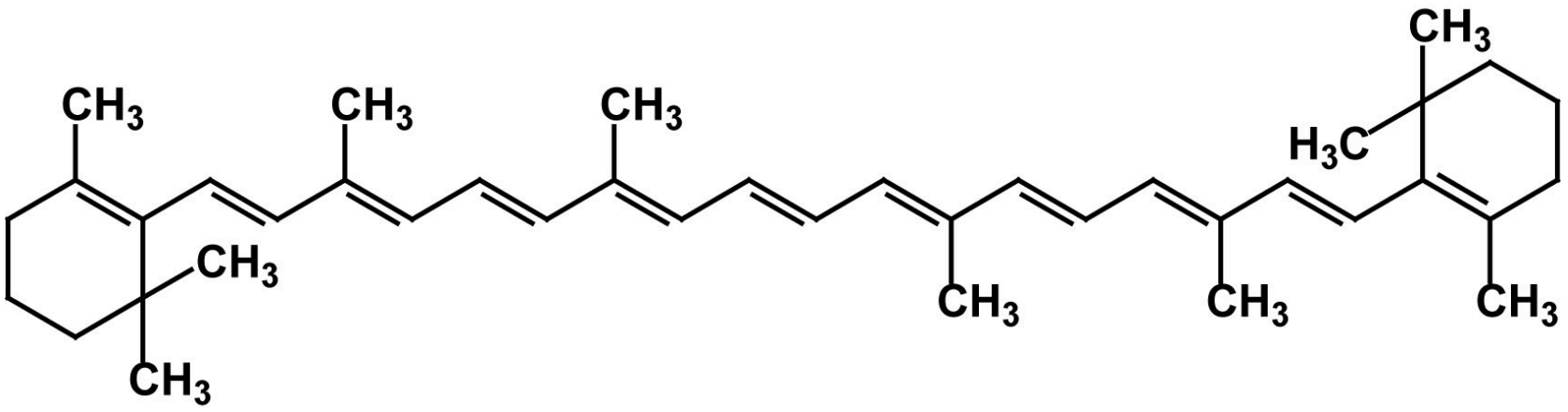
Lab 4. Is β-Carotene a conjugated diene?

Predict λ_{max} using _____ Rules (observed λ_{max} = 452 nm)



Lab 4. Is β-Carotene a conjugated diene?

Predict λ_{max} using Feiser-Kuhn Rules (observed λ_{max} = 452 nm)



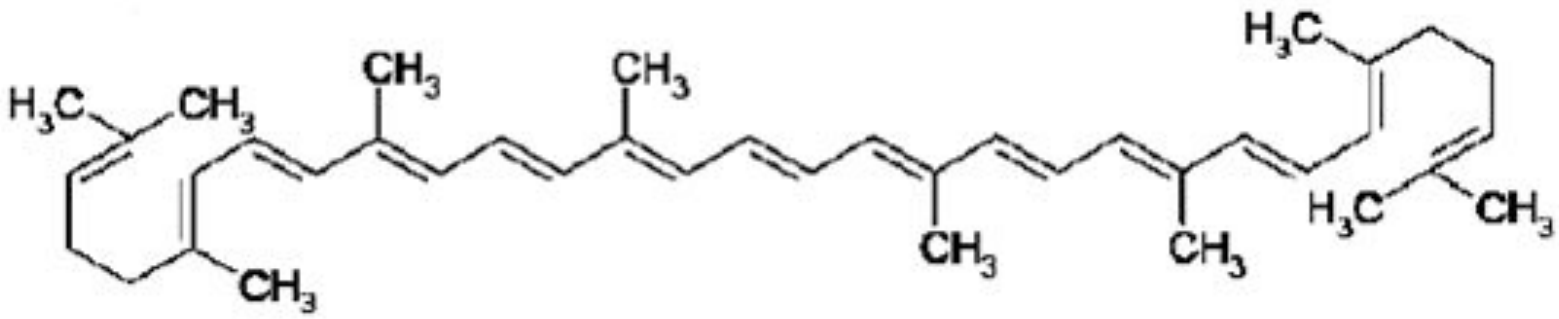
$$\lambda_{max} = 114 + 5M + n\,(48.0 - 1.7\,n) - 16.5\,R_{endo} - 10\,R_{exo}$$

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

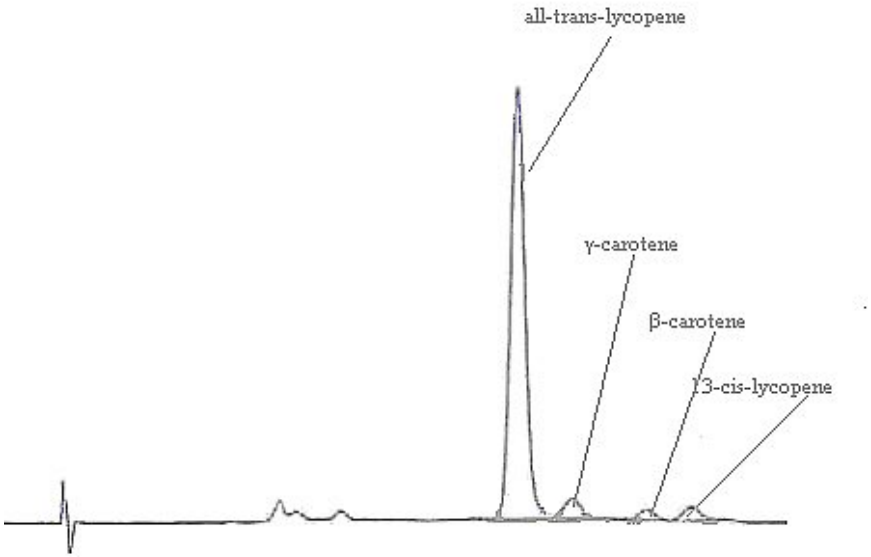
$$= 453.3 \text{ nm (vs. observed } \lambda_{max} = 452 \text{ nm)}$$

Lab 4. Is Lycopene a conjugated diene?

Predict λ_{max} using _____ Rules (observed λ_{max} = 474 nm)



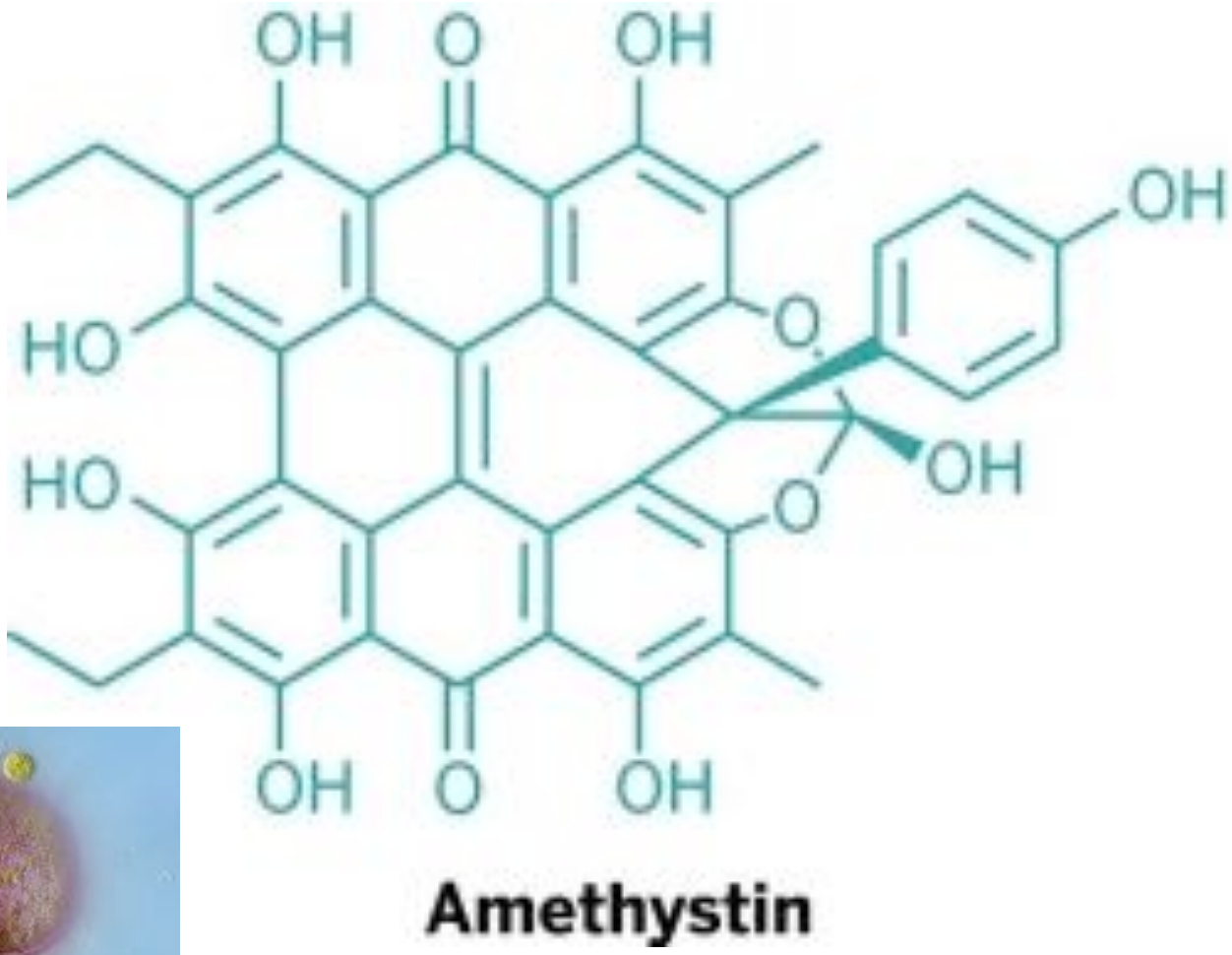
http://www.organic-herb.com/Product/Item/75.html



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)

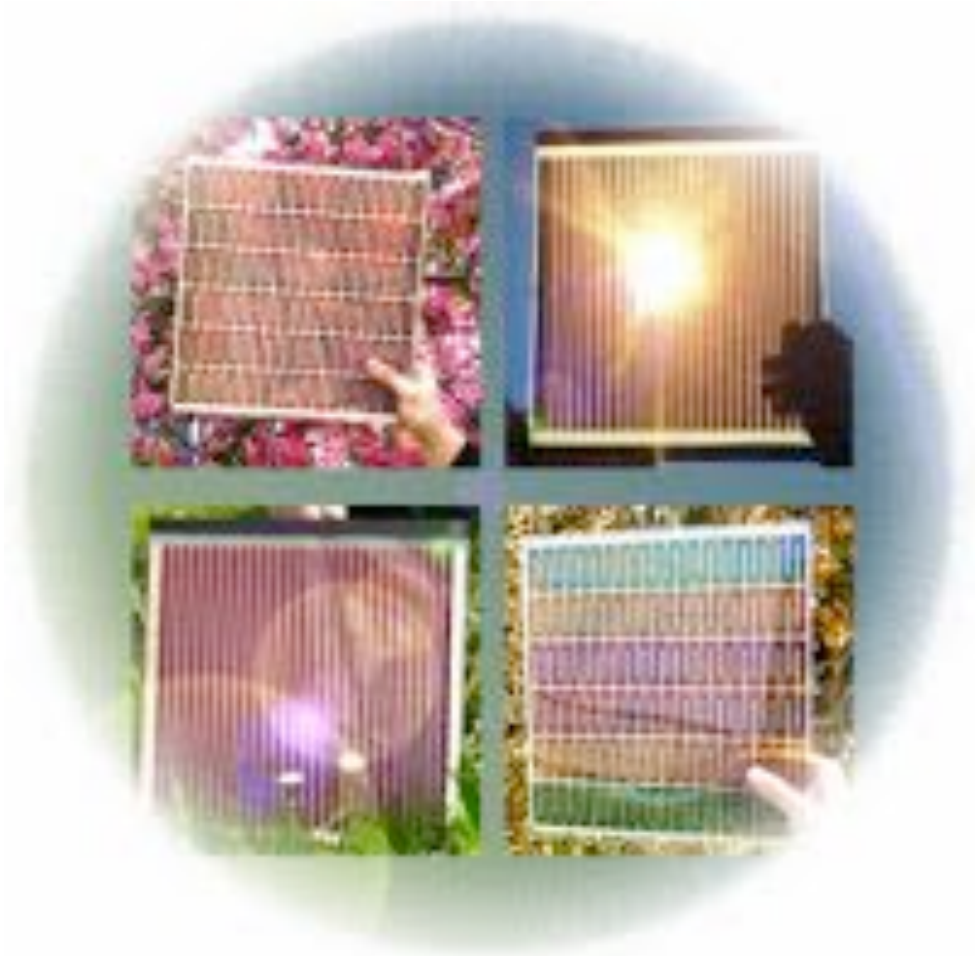
Predict
λ_{max}



Amethystin

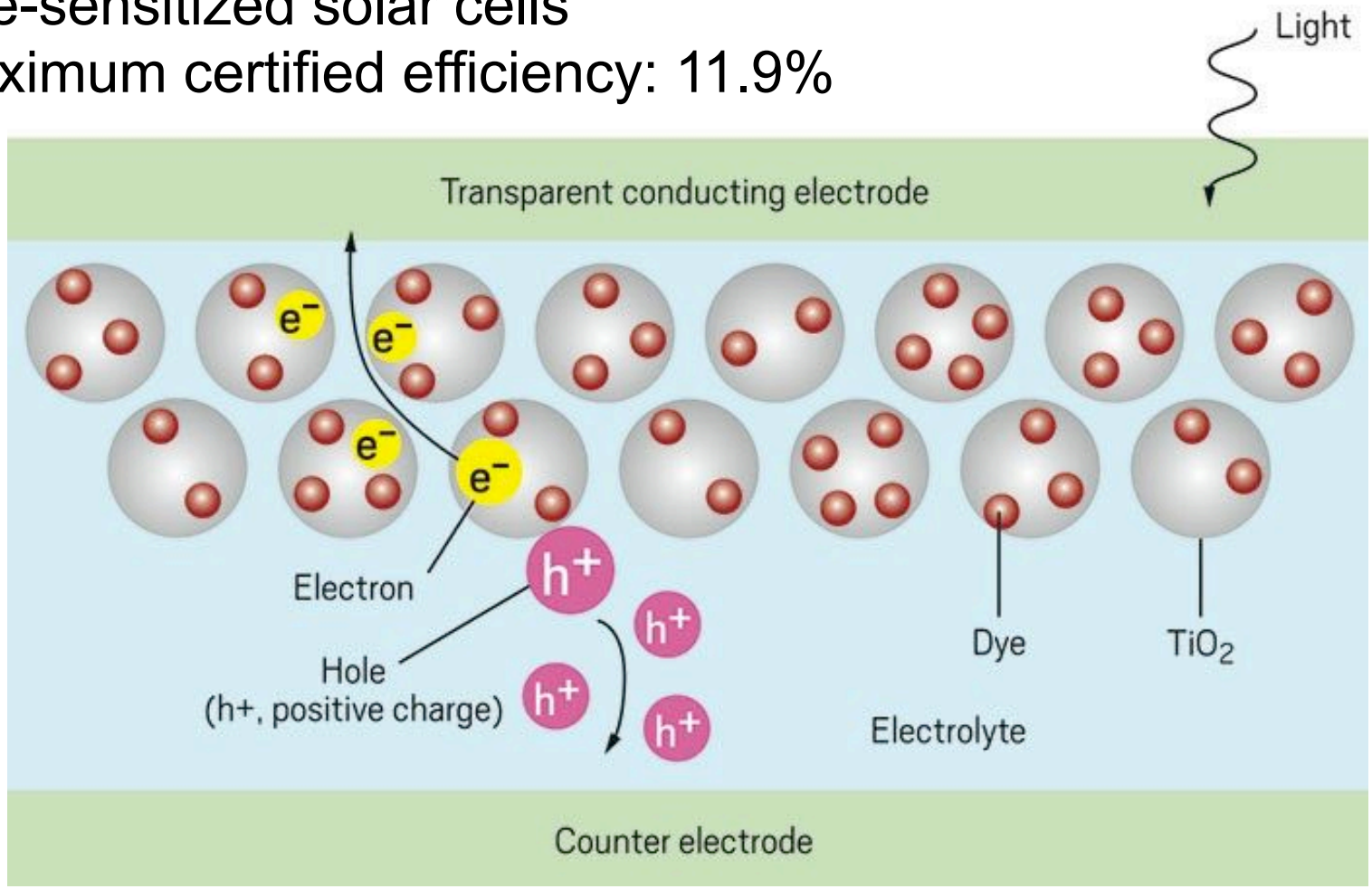
Stentor amethystinus

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

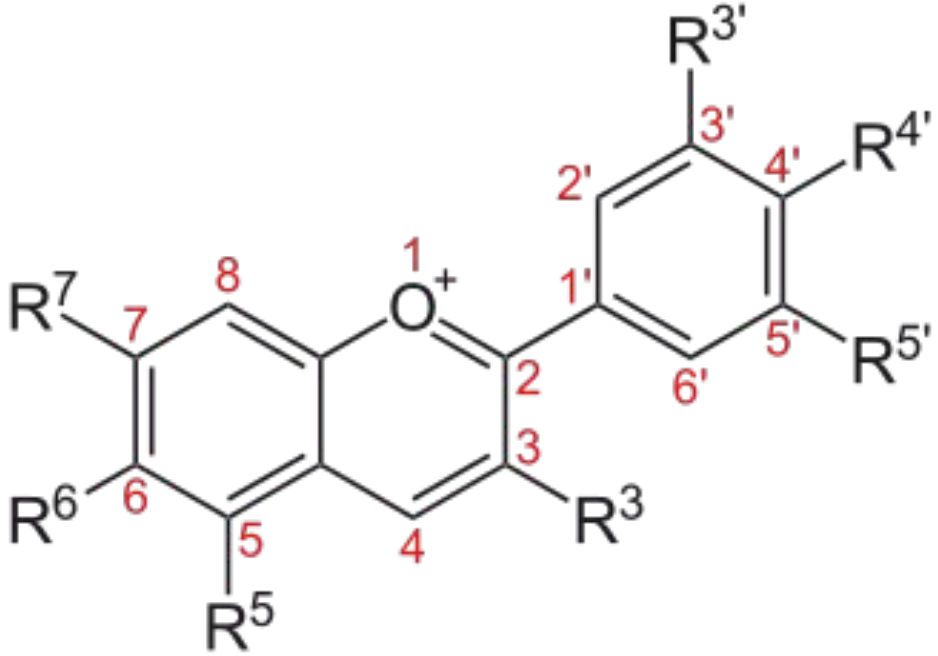
Dye-sensitized solar cells
Maximum certified efficiency: 11.9%



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)

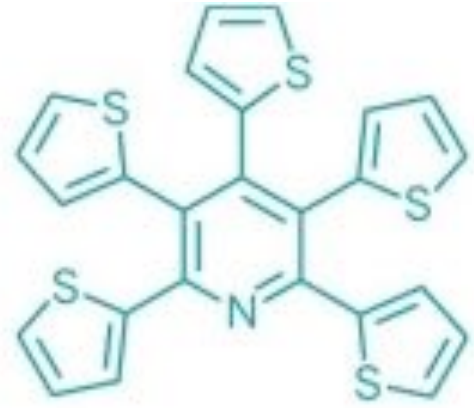
Are anthrocyanins (purple and blue) conjugated dienes?

https://en.wikipedia.org/wiki/Anthocyanin

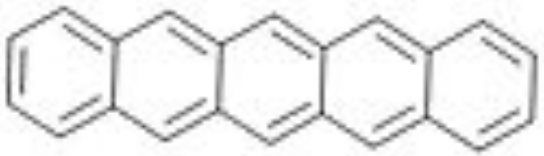


May help reduce risk of cancer, stroke, and heart disease.

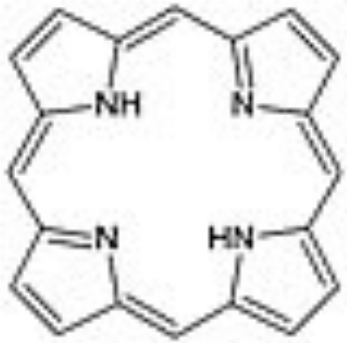
OLED (Organic Light Emitting Diodes): are these compounds conjugated?



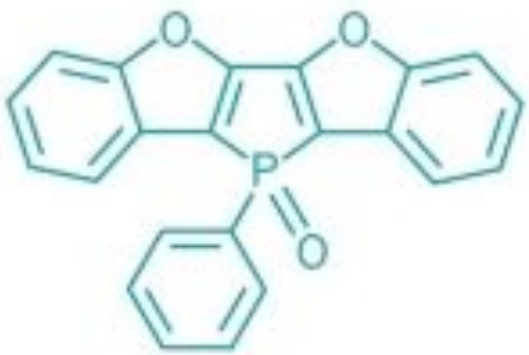
Penta(2-thienyl)pyridine



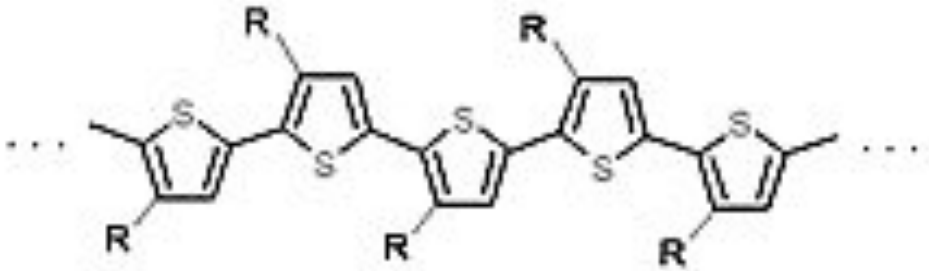
Pentacene



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

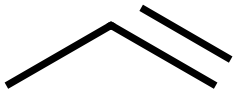
Isolated Dienes: less stable
2 C=C separated by More Than 1 C-C

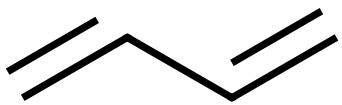
Cumulated Dienes: least stable.
2 adjacent C=C

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 π electrons?

A Conjugated Diene has Delocalized π electrons





C-C length	153 pm	151 pm	148 pm
C=C length		134 pm	

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

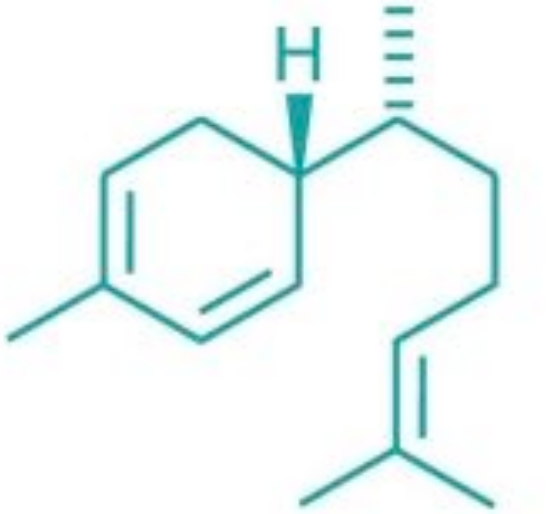
Which pi bond is the most reactive? Why?

http://cen.acs.org/articles/90/i48/Tomato-Defense-Weapons.html

11/26/12, CEN, p. 31 "Tomato Defense Weapons"

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.



7-Epizingiberene

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

Draw **all** possible products of this reaction.

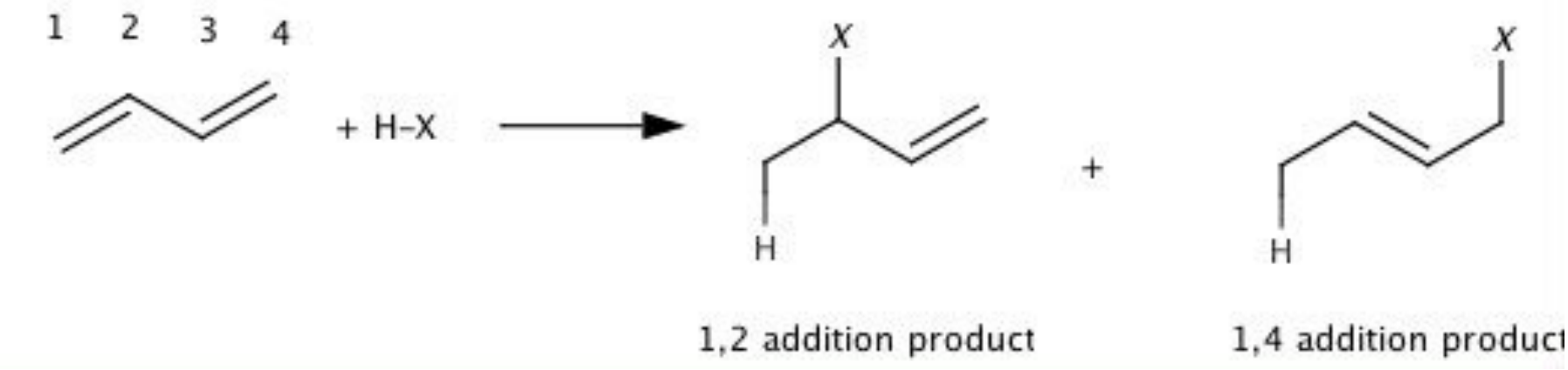
Use curved arrows to show how each product is formed.

Which product is the most likely product? Why?

Dienes Undergo Addition Reactions

Conjugated Dienes React Like Alkenes but with a "Twist"

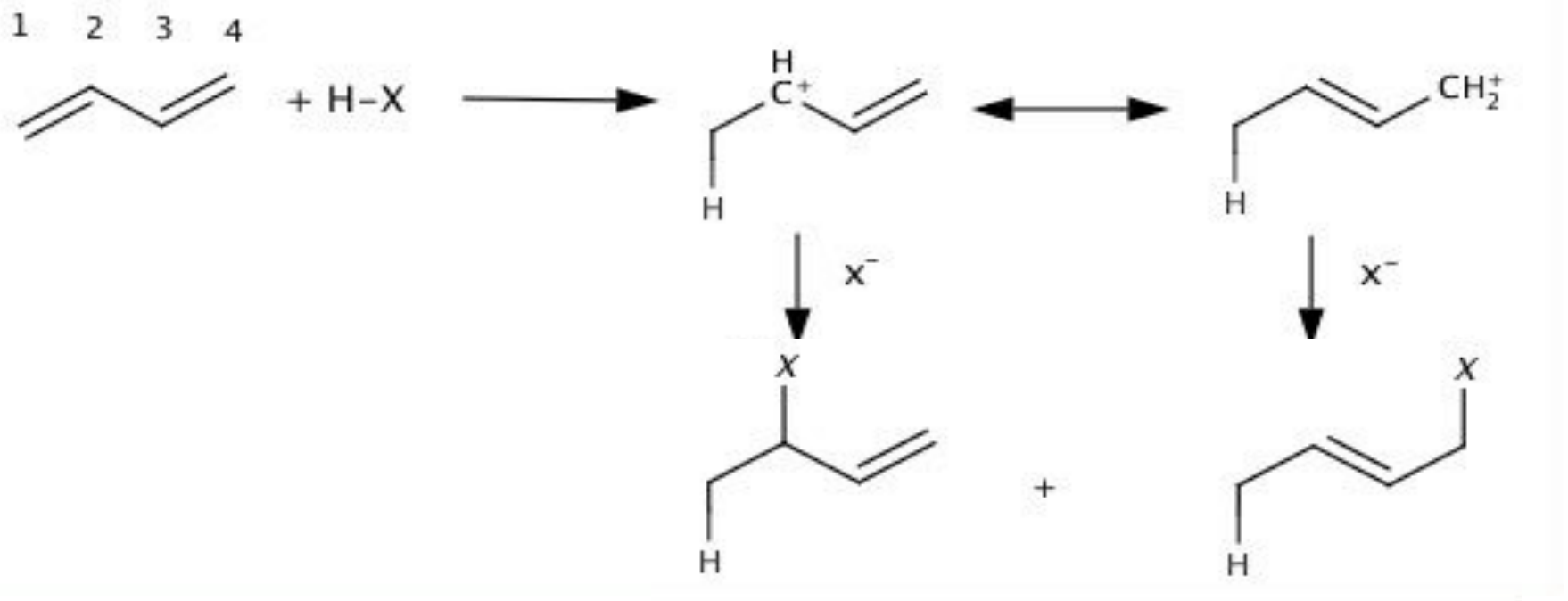
Addition of HX to Conjugated Diene Produces Two R-X Products: 1, 2 Addition and 1, 4 Addition Products



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



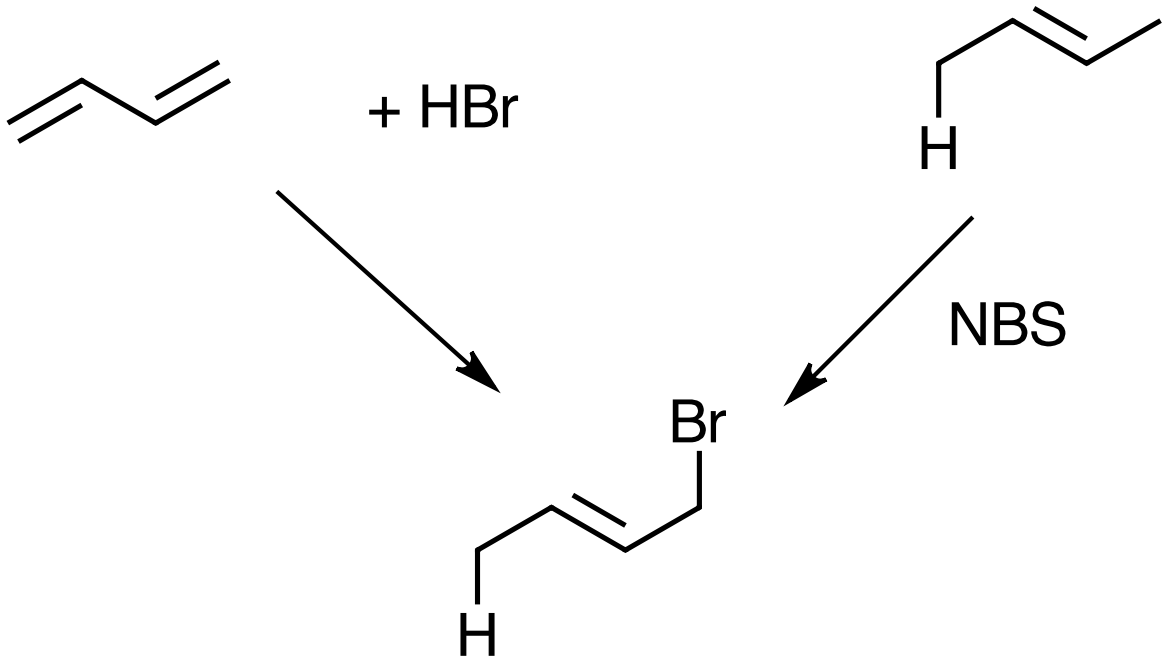
1,2 product 1,4 product

Which C^+ intermediate is more stable?

Which product is more stable?

Addition of HX to Conjugated Diene forms Allylic Halide

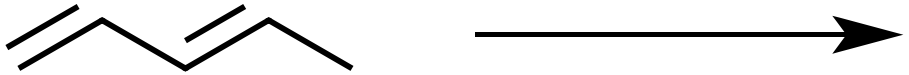
Two ways to synthesize 1-bromo-2-butene.

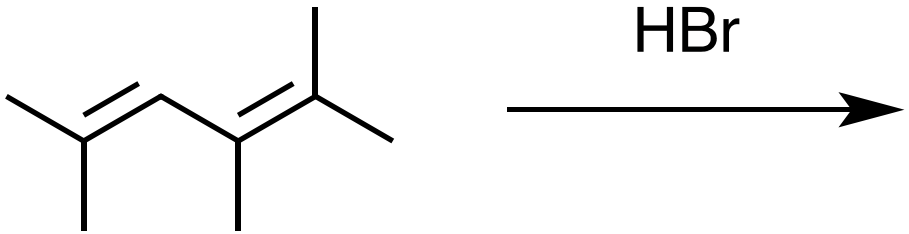


Alkene + NBS + hν forms Allylic Bromide (Klein, p. 512)
See Chem 12A

Which method is better?

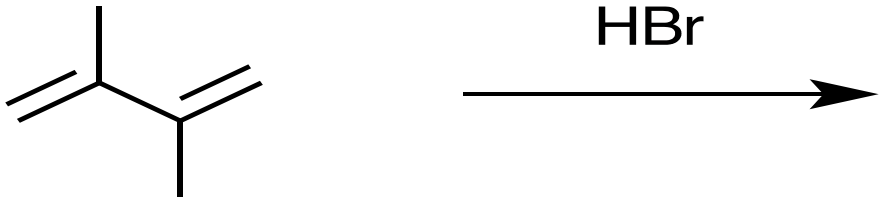
Predict the product(s) of each reaction:

a. 

b. 

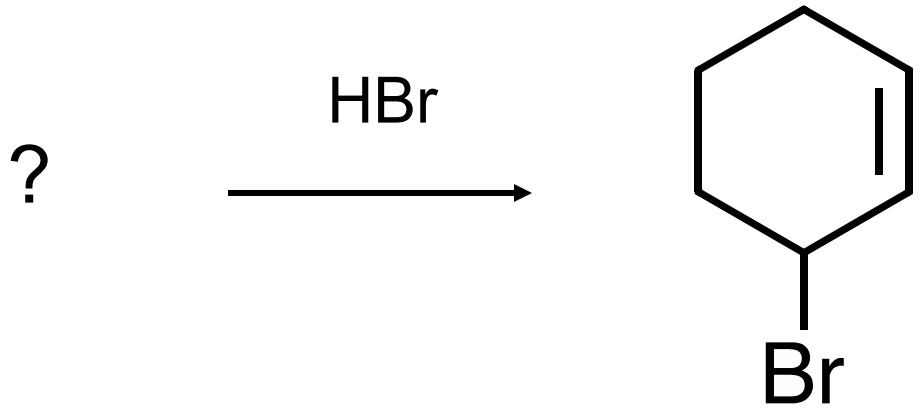
See Practice Problems

One diene produces 4 products whereas the other diene produces 2. Explain.



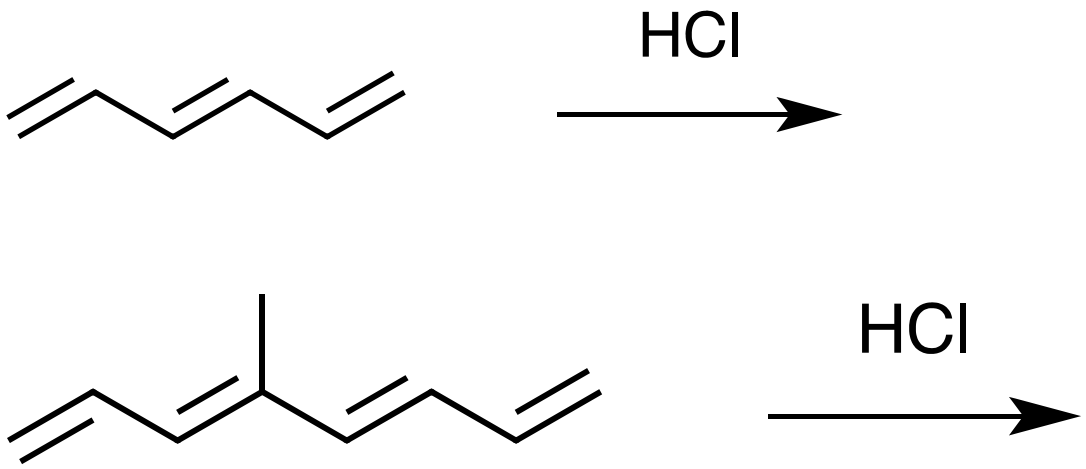
See Practice Problems

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



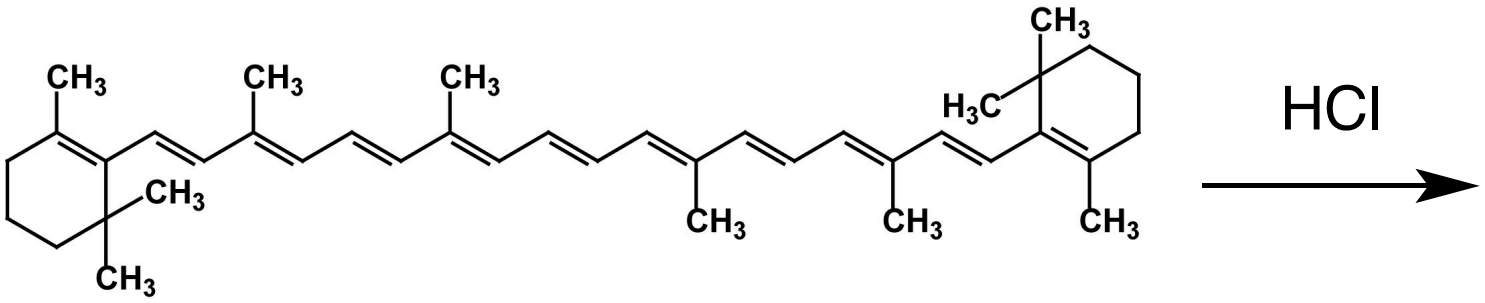
Conjugated diene → 1,2 product and 1,4 product

Conjugate triene → 1,2 product and 1,4 product and ??

Conjugate tetraene → 1,2 product and 1,4 product and ??

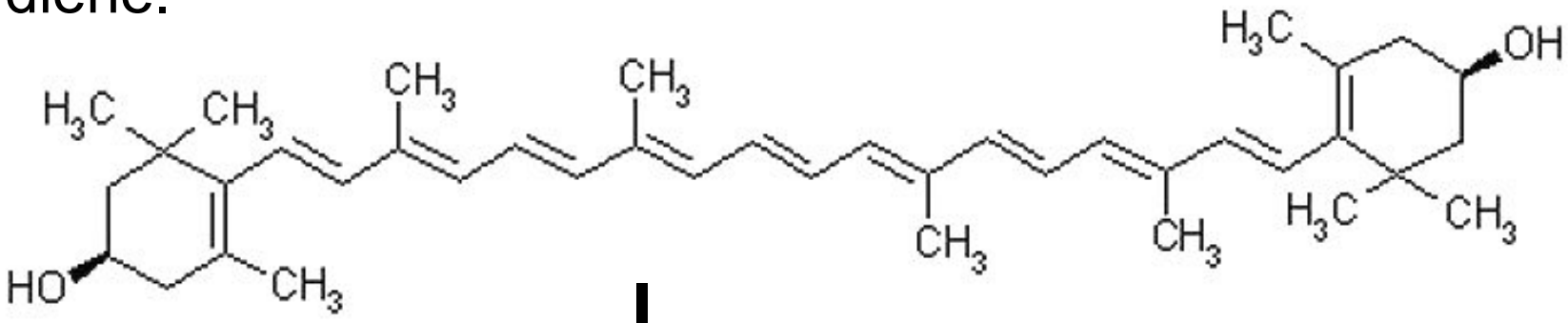
Lab 4: Conjugated Polyenes are found in Plant Pigments

Does Carotene undergo addition?

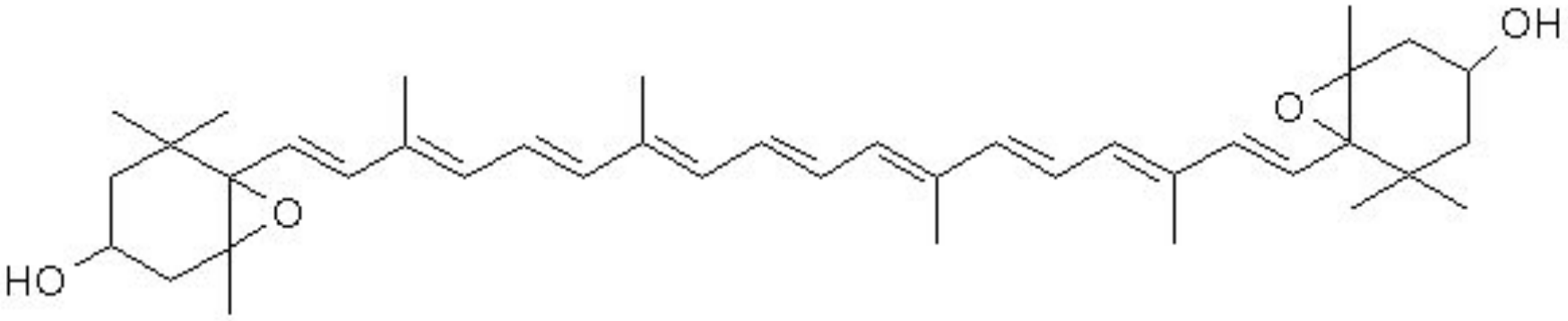


How many pi bonds are conjugated?
How many possible products?

Zeaxanthin (very common carotenoid alcohol found in nature) is a _____ diene.



Reaction conditions?



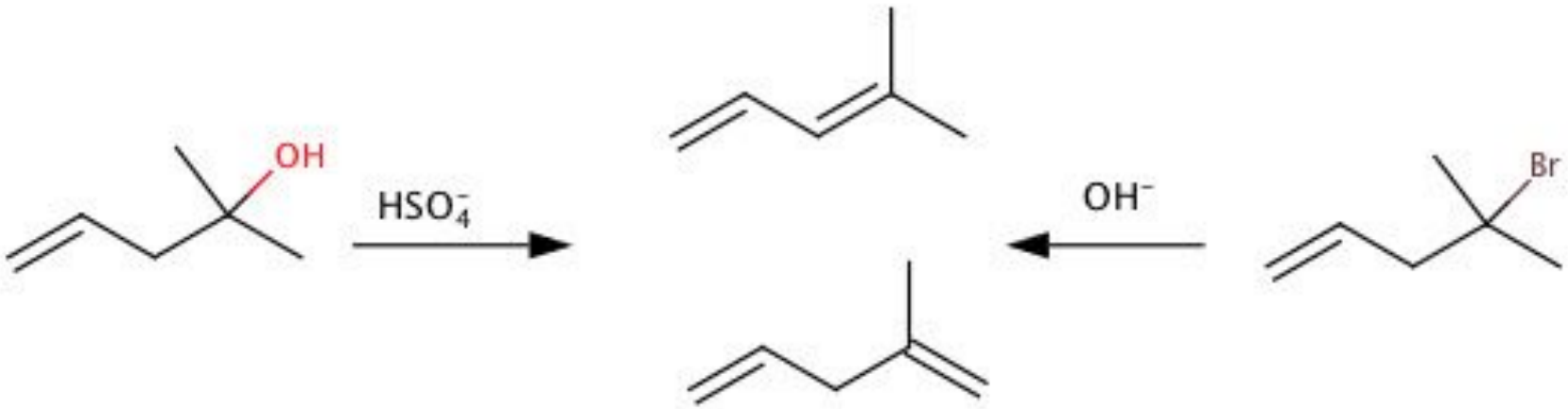
Violaxanthin (type of Xanthophyll) is a _____ diene.

Orange pigment found in many plants, e.g., pansies.

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

Objective: How are dienes prepared?

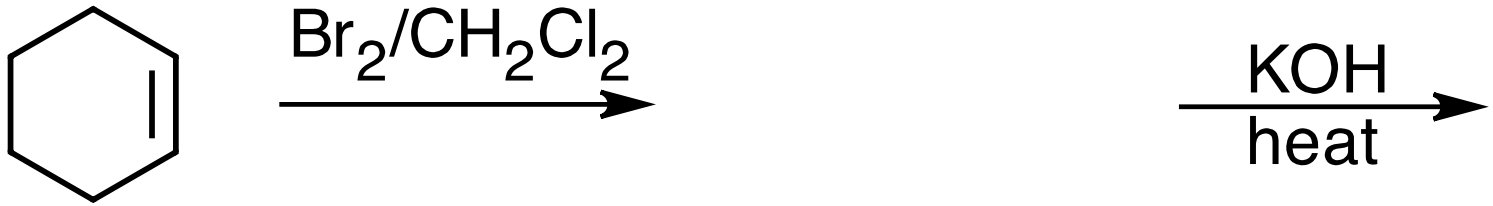
Dienes are Prepared from an Alkene with a Leaving Group
The LG is Involved in an Elimination Reaction
Where should the LG be relative to the π bond to make a conjugated diene?



The more stable product is formed. Which product is more stable?

Objective: Predict the product of each reaction

cyclohexene reacted with Br_2 / CH_2Cl_2 then with KOH / heat

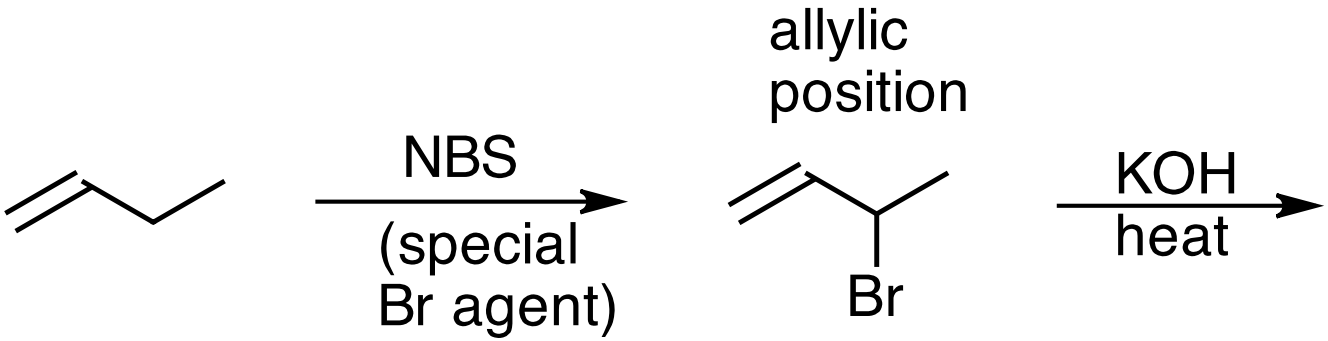


What does pi bond do?
Is Br_2 a $Nu:^-$ or E^+?

What does KOH do?

Objective: Predict the product of each reaction

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

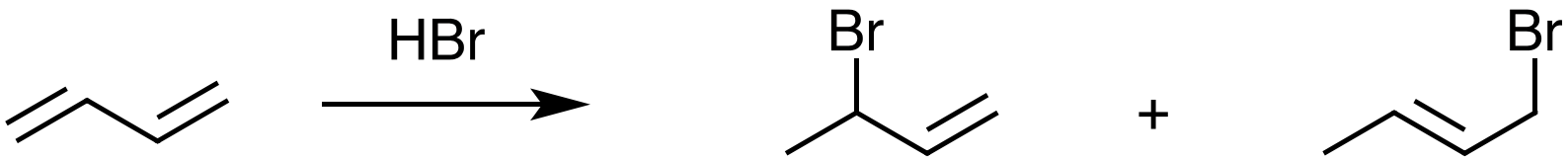


ID structural features
What does KOH do?

1,3-butadiene + HBr -->

1,2 product vs. 1,4 product

Reaction Temperature Determines Product Distribution



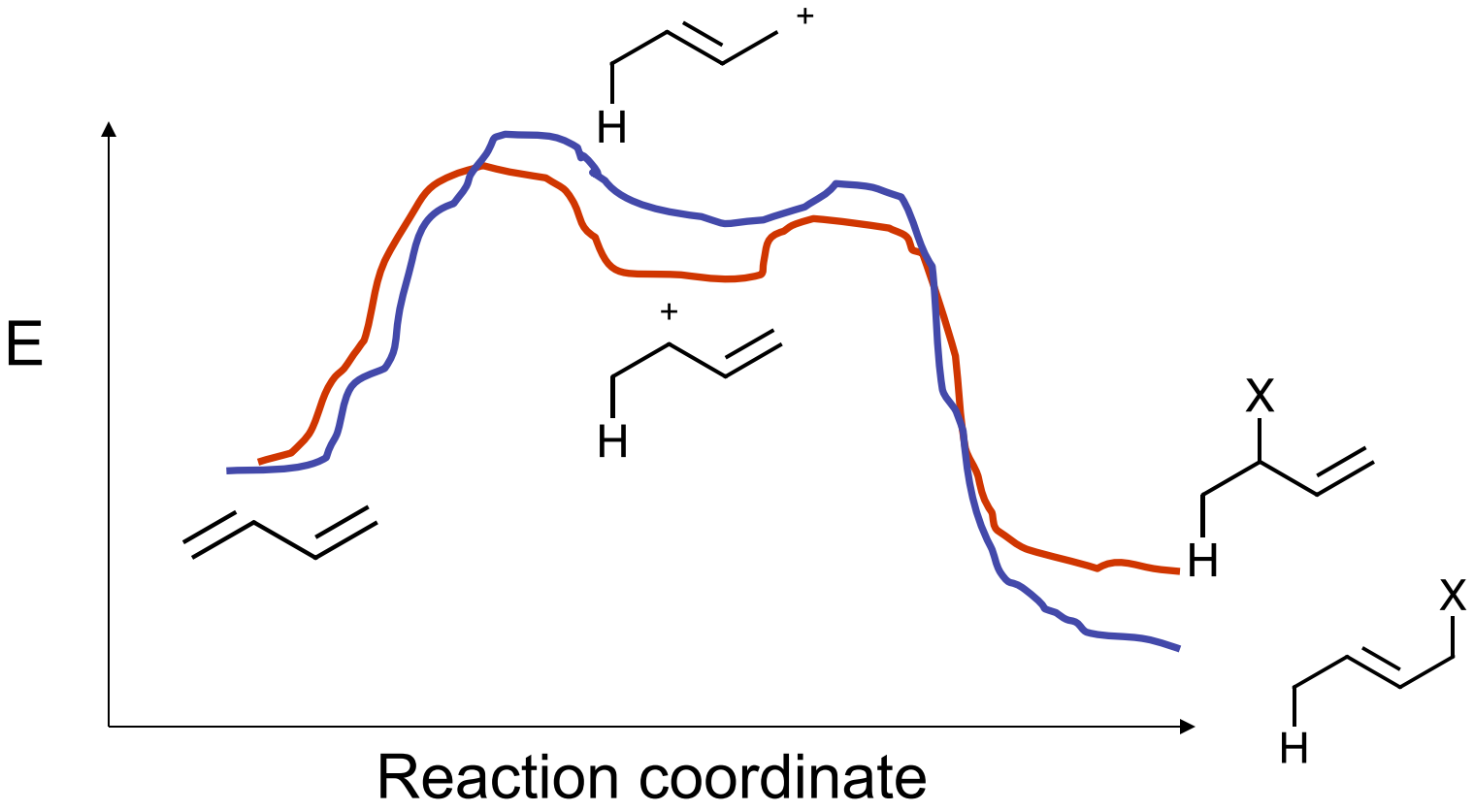
T = 0°C	71%	29%
T = 40°C	15%	85%

Structural feature of products: allylic bromide

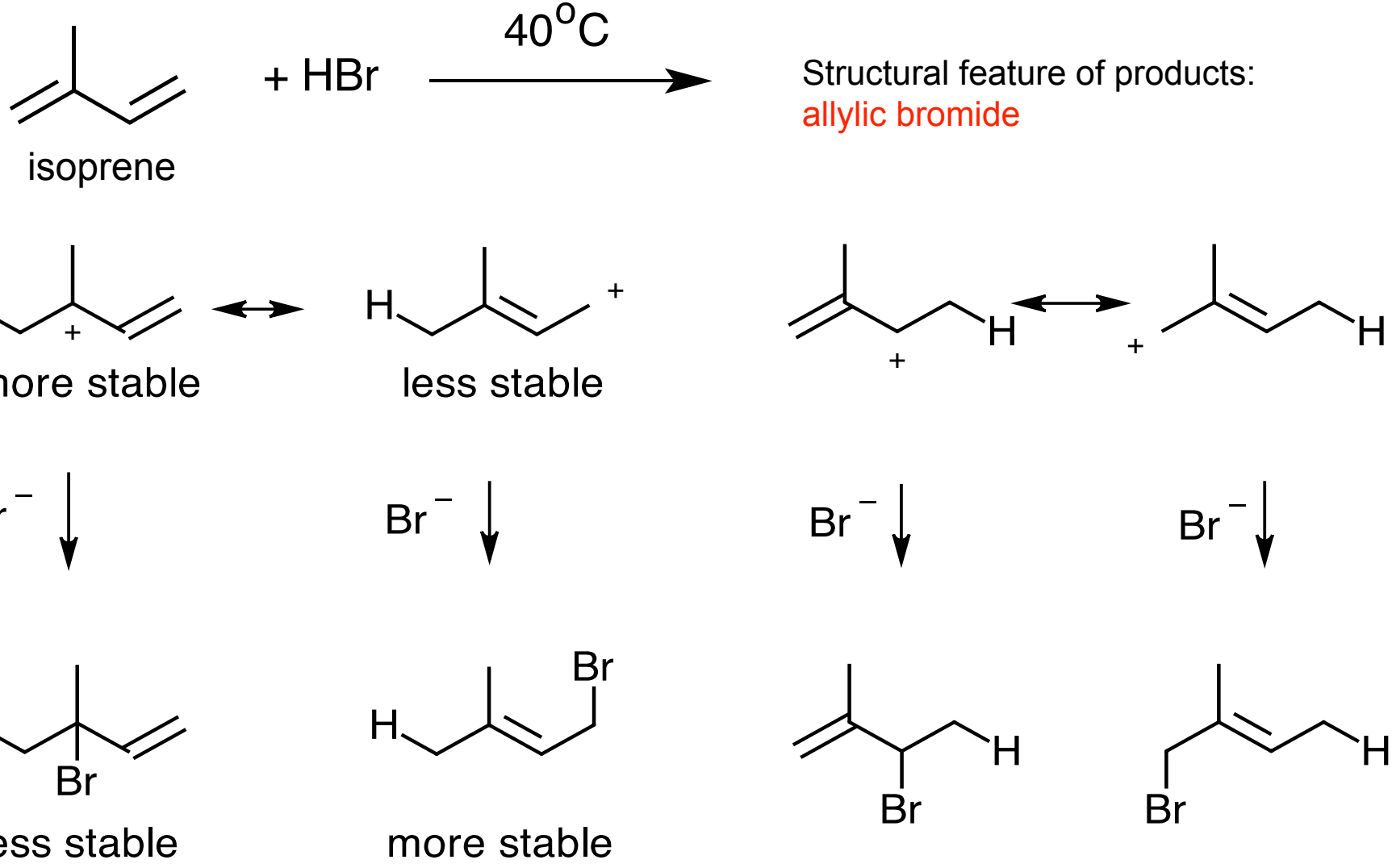
Reaction Temperature Determines Product Distribution

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

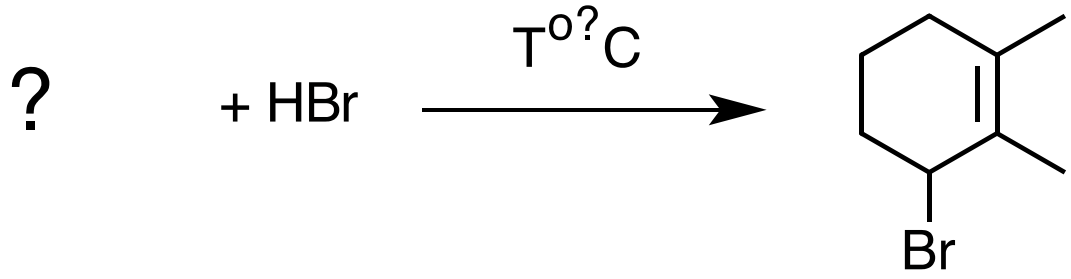
High T (40°C) ==> Less stable intermediate ==> More stable product (Thermodynamic Control)



Objective: Predict the product or ID the reaction conditions



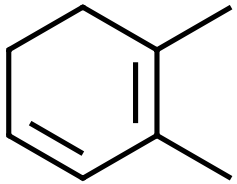
Objective: Predict the product or ID the reaction conditions



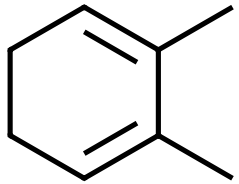
Identify structural features of product: allylic bromide

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

Is reactant A or B?

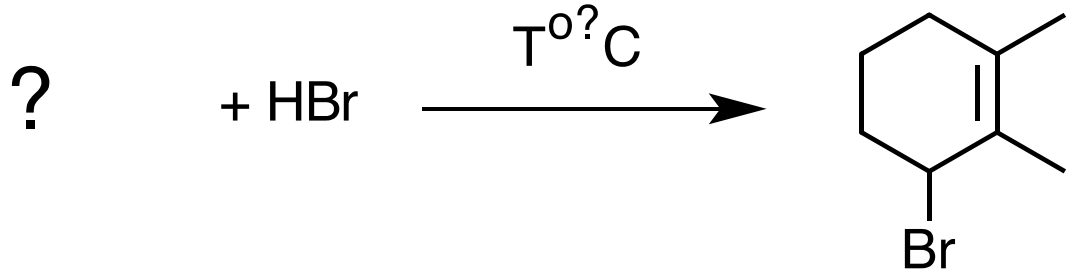


A



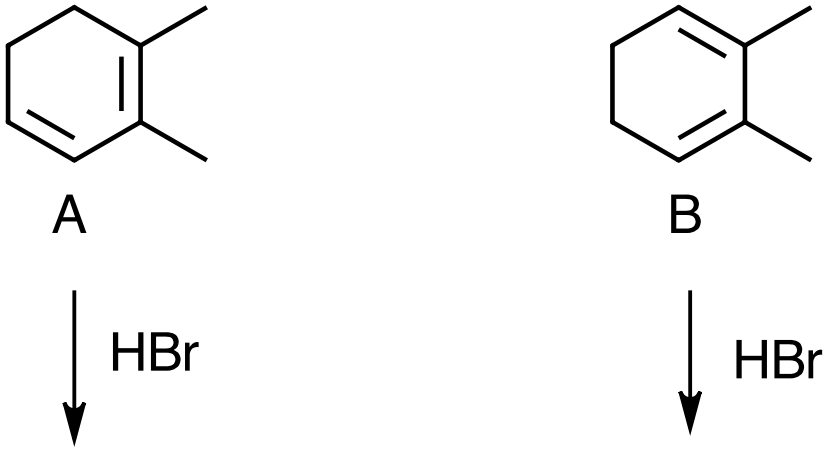
B

Objective: Predict the product or ID the reaction conditions



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

Is reactant A or B?

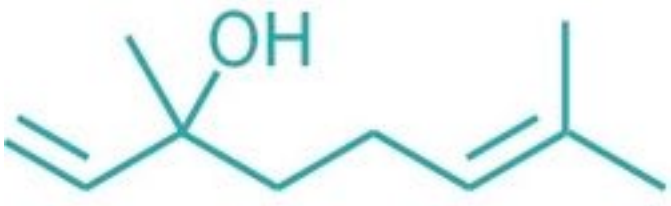


Predict products at high and low T

Lavendar oil – fragrance, antiseptic, and antioxidant contains linalool (terpene)

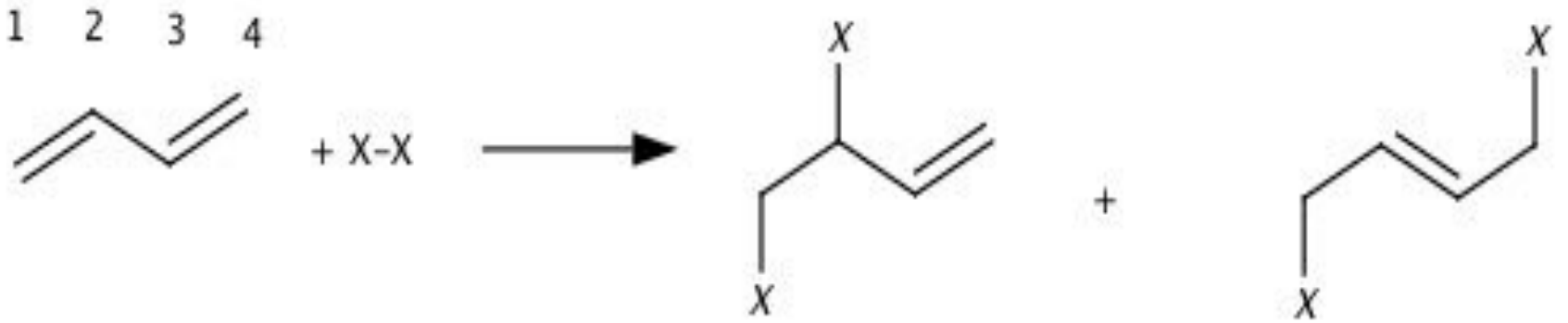
http://cen.acs.org/articles/92/i41/Problem-Lavender-Oil.html

What starting material would you use to make linalool?

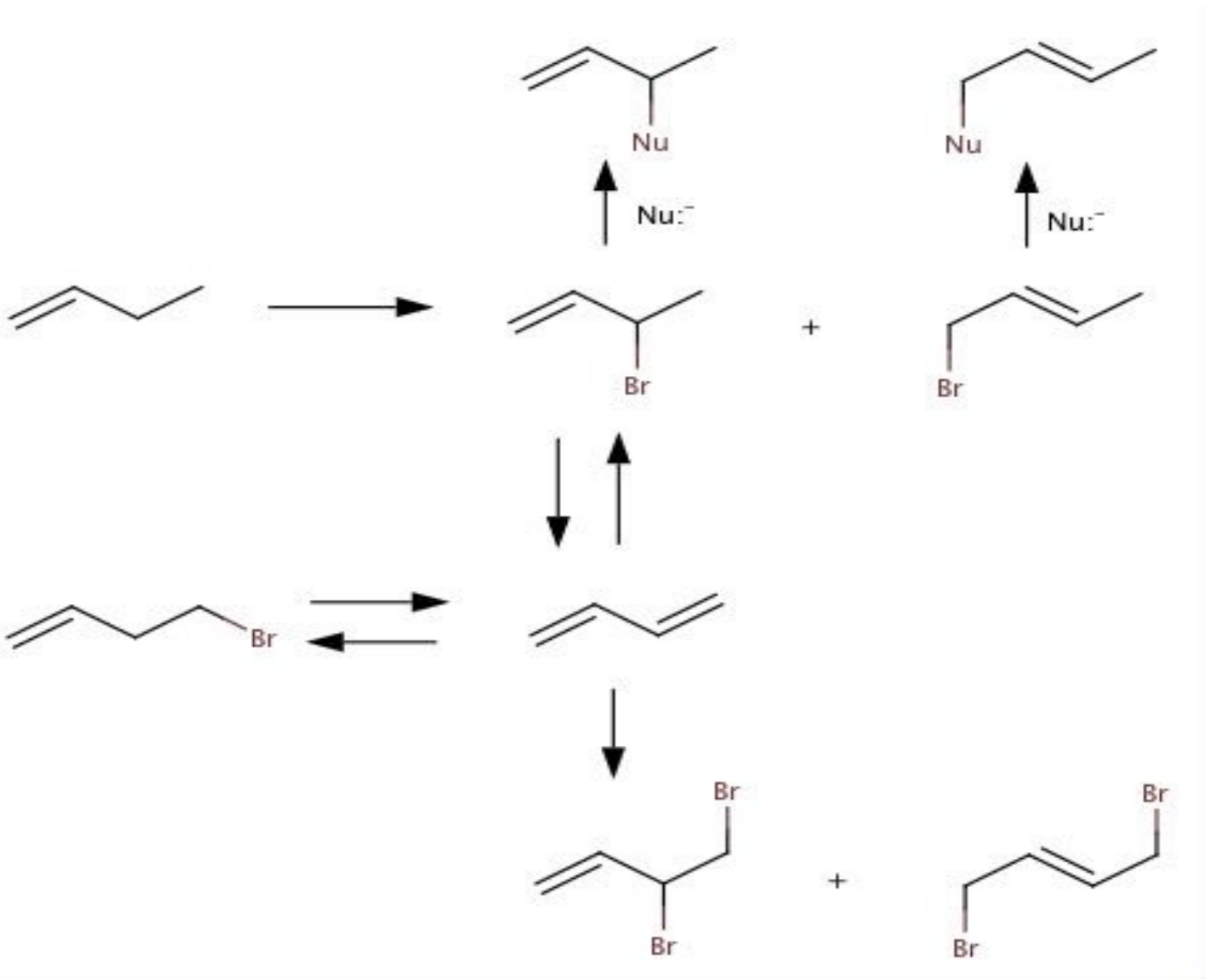


Linalool

Addition of X_2 to Conjugated Diene Tends to Form 1, 4 Addition Product

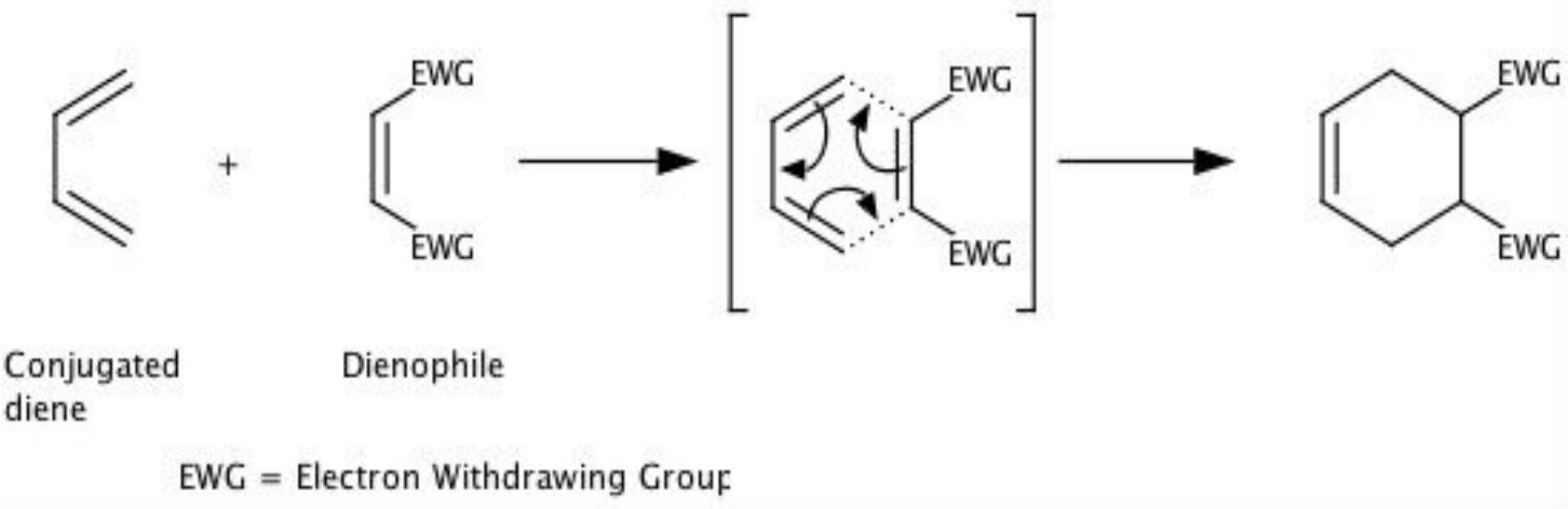


Add Allylic and Diene Reactions to your Organic Reaction Map



Diels-Alder Reaction: Make a Ring from a Chain

Conjugated Diene + Dienophile --> Ring

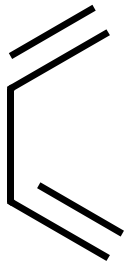


Electron Withdrawing Groups (EWG): NO_2, CN, COOH, CHO

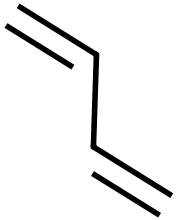
What makes a group an EWG?

Reaction occurs in ***ONE*** step: no reaction intermediates detected ==> **Pericylic** Mechanism

Two conformations for conjugated dienes:

s-cis 

Need s-cis for Diels-Alder reaction

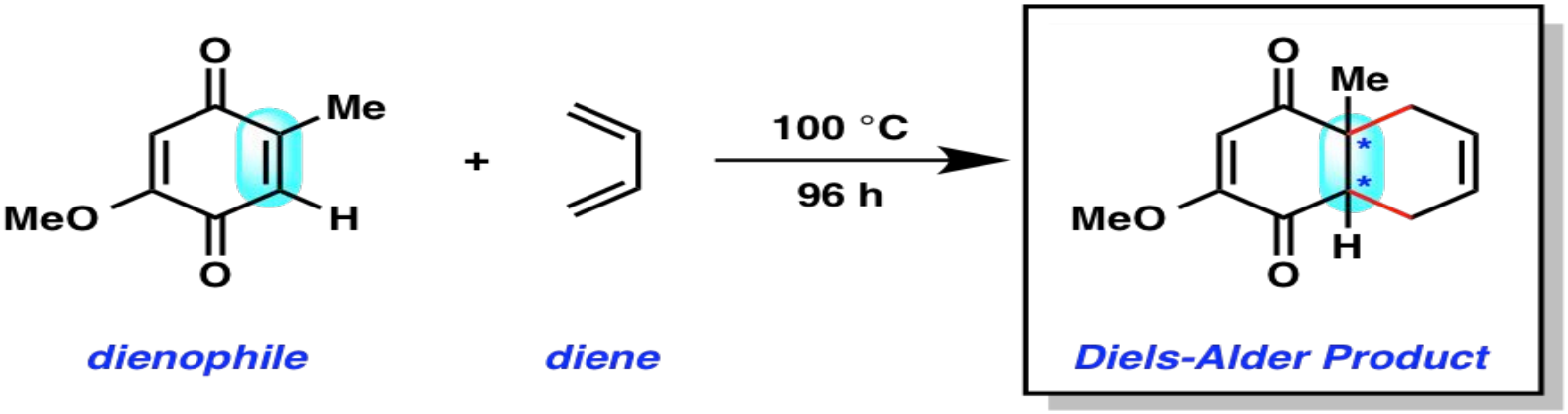
s-trans 

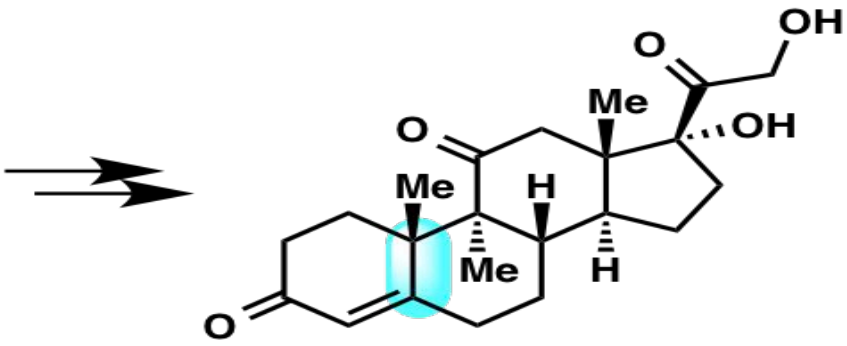
s refers to rotation about a sigma (σ) bond

Which conformer is more stable? s-cis s-trans

Diels-Alder involved in Cortisone synthesis (LearnBacon.com)

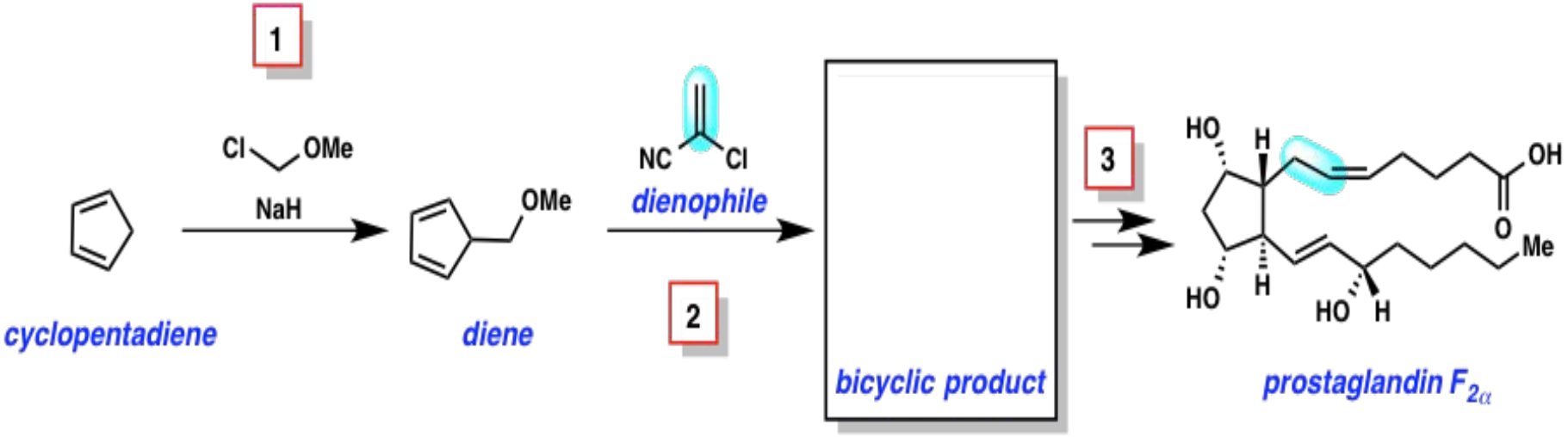
Cortisone used to treat inflammation but side effects include hyperglycemia, anxiety/depression, glaucoma, and osteoporosis.





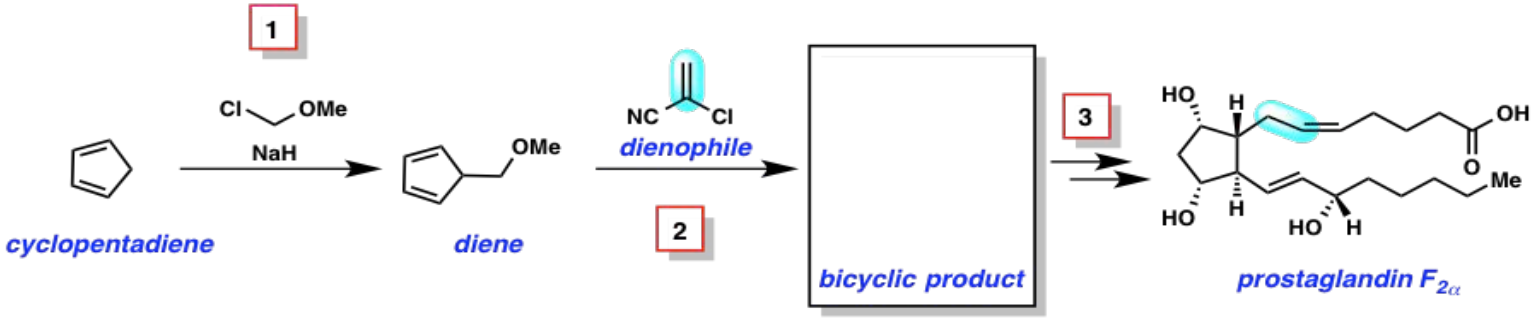
adrenal gland hormone
treatment of inflammation

Diels-Alder used to make prostaglandin F2-alpha – used to induce labor in pregnant women. (LearnBacon.com)

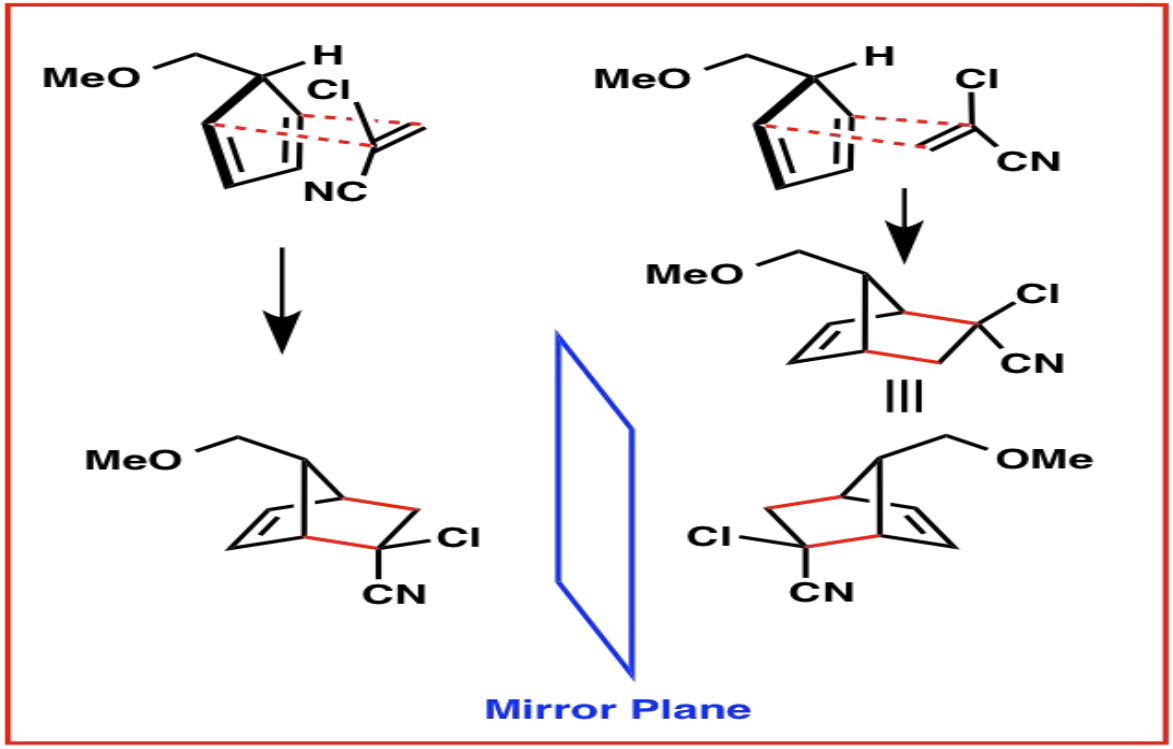


What is the structure of the bicyclic product?

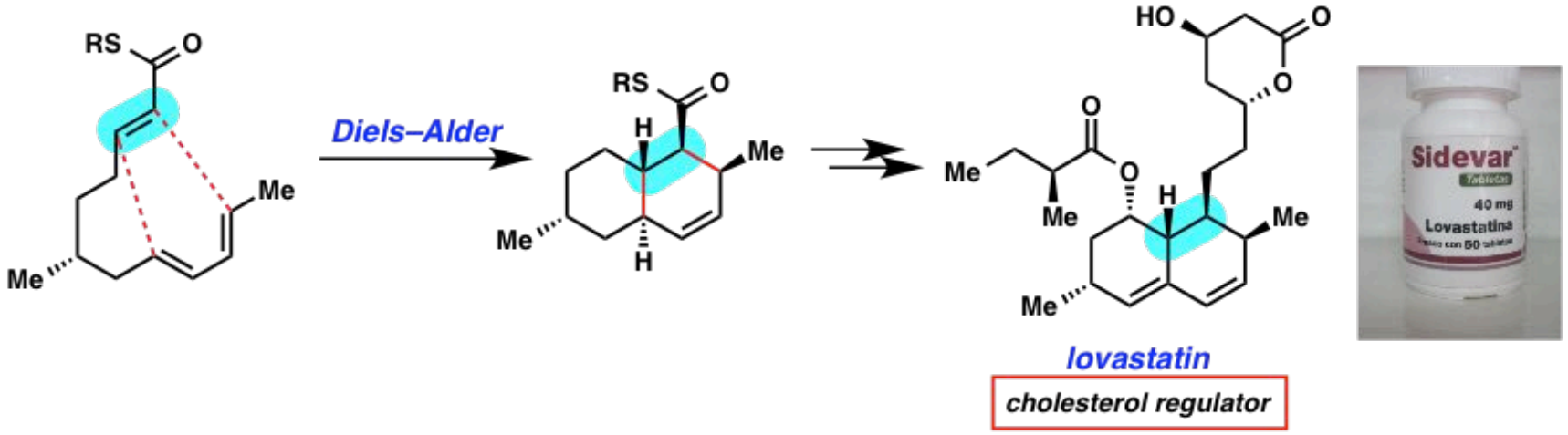
Diels-Alder used to make prostaglandin F2-alpha – used to induce labor in pregnant women. (LearnBacon.com)



What is the structure of the bicyclic product?

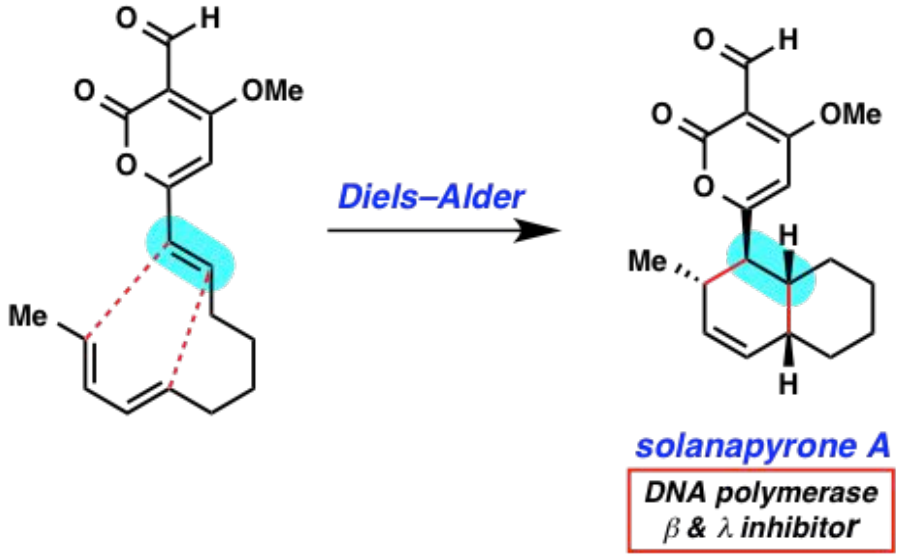


Intramolecular Diels-Alder reactions: synthesis of Lovastatin (cholesterol lowering drug) and biosynthesis of solanapyrone A (DNA polymerase inhibitor). (LearnBacon.com)



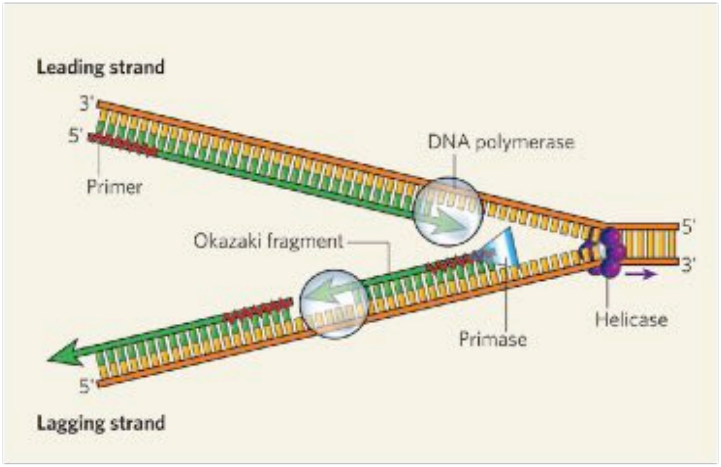
lovastatin

cholesterol regulator

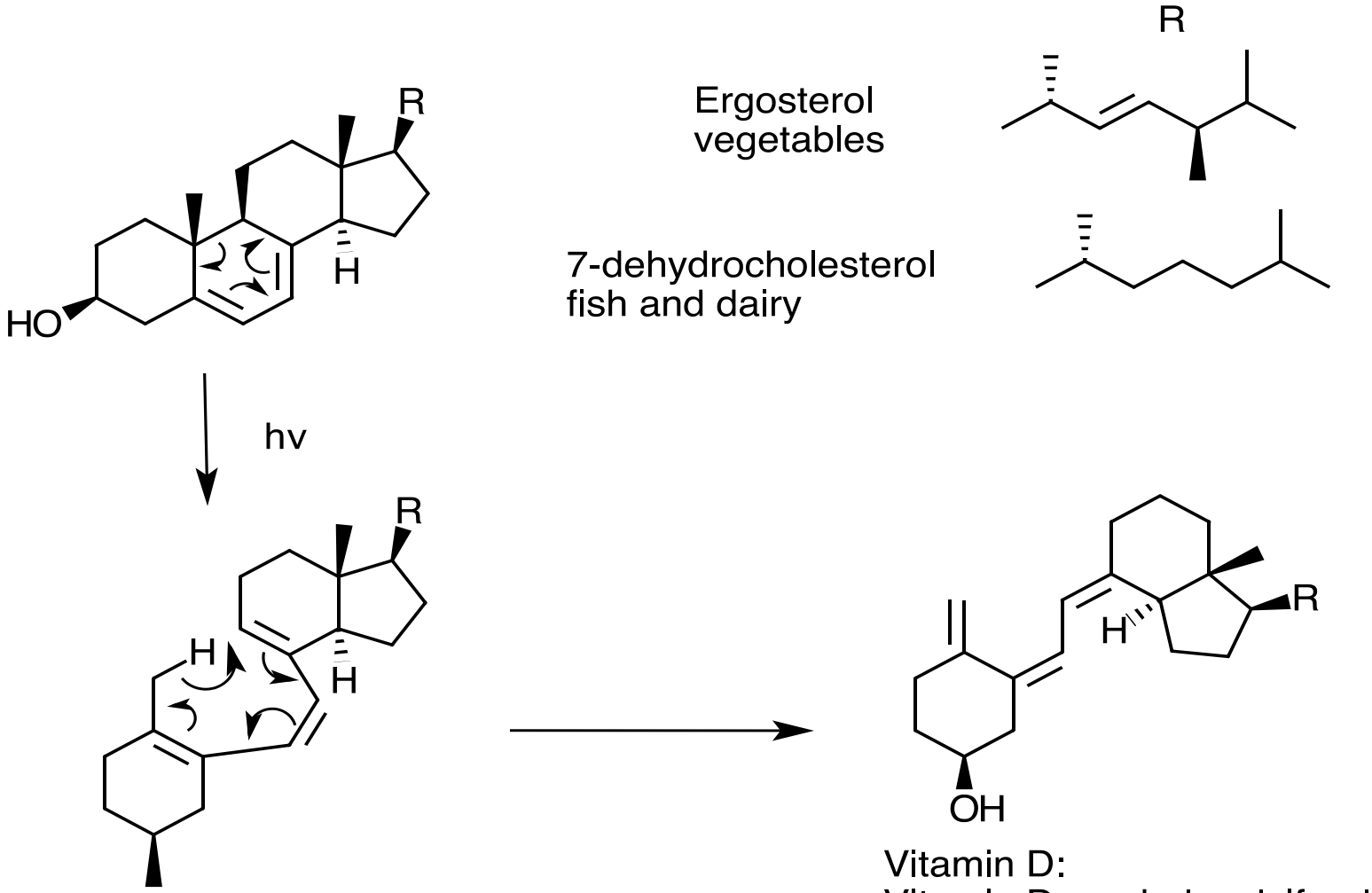


solanapyrone A

DNA polymerase β & λ inhibitor



Vitamin D biosynthesis involves a Pericyclic Reaction (Klein, p. 800)

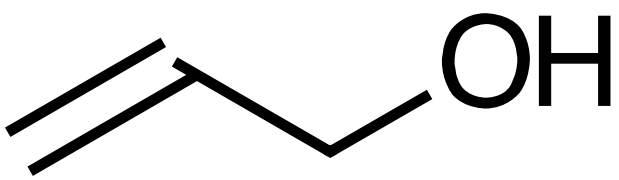


Vitamin D:
Vitamin D_3 = cholecalciferol
Vitamin D_2 = ergocalciferol

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

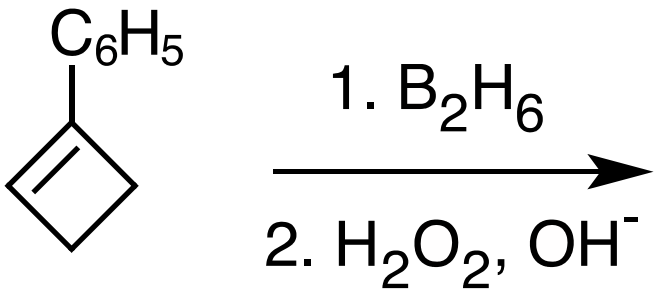


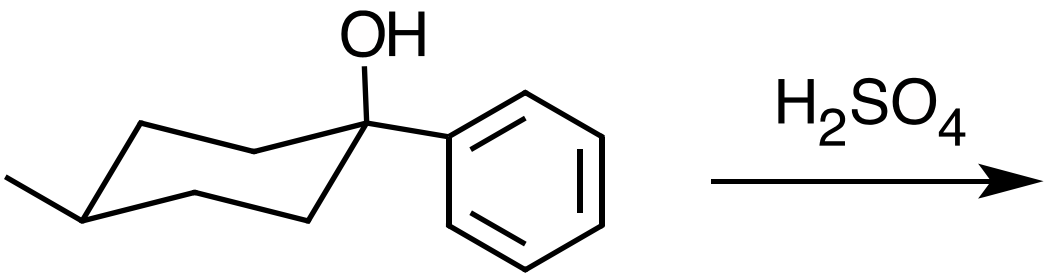
2. Suggest a reasonable explanation for the following observation:

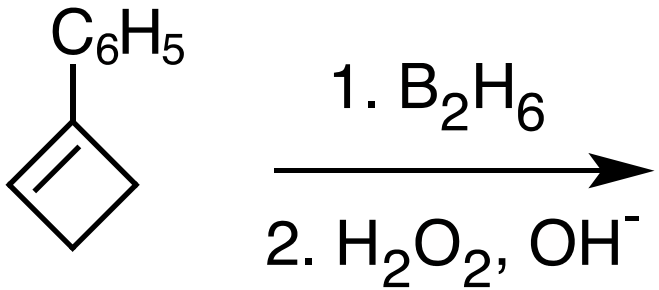
After a solution of 3-buten-2-ol in aqueous sulfuric acid had been allowed to stand for 1 week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol.

Problem solving steps: 1. Identify functional group(s)
2. Relate reaction conditions to reaction type

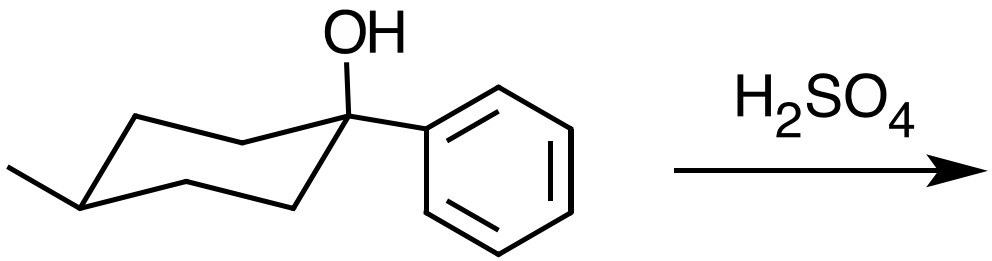
Determine the product of each reaction:







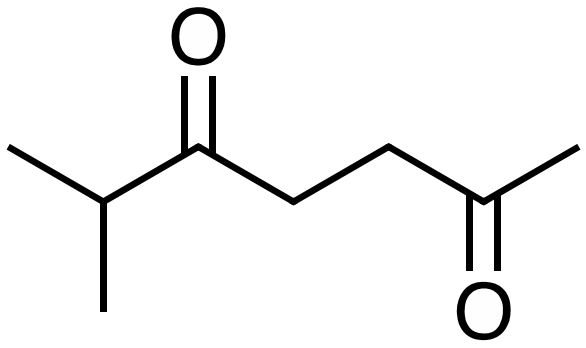
FG = alkene
Conditions: addition to make alcohol, non-Markovnikov

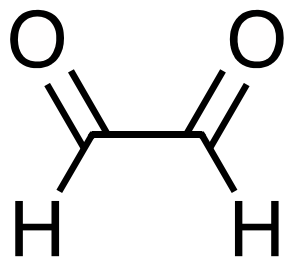


FG = alcohol
Conditions: elimination to make alkene

Problem solving steps: 1. Identify functional group(s)
2. Relate reaction conditions to reaction type

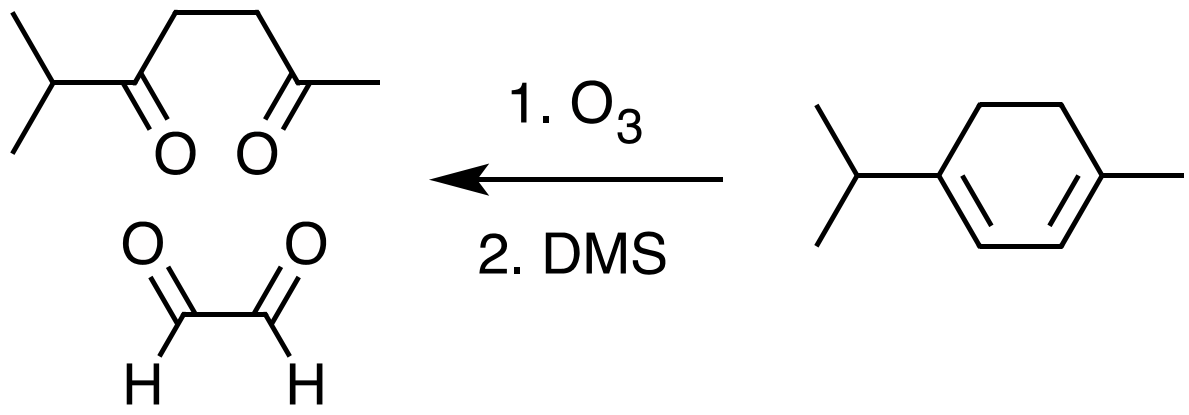
α-Terpinene is a pleasant smelling compound present in the essential oil of marjoram. α-Terpinene undergoes hydrogenation with 2 equiv of H_2 to produce 1-isopropyl-4-methylcyclohexane. Ozonolysis of α-Terpinene yields the following two compounds:





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

What is the structure of α-Terpinene?



FG = ketone/aldehyde
Conditions: alkene bond cleavage