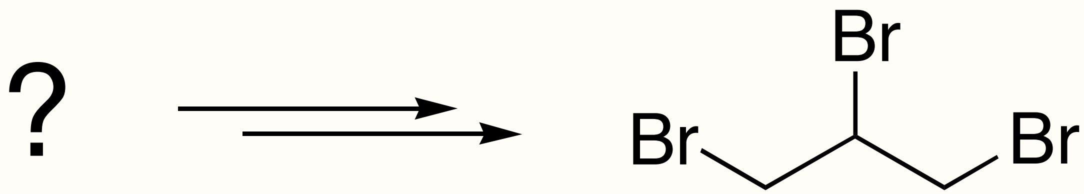
Lecture 22
Organic Chemistry 1

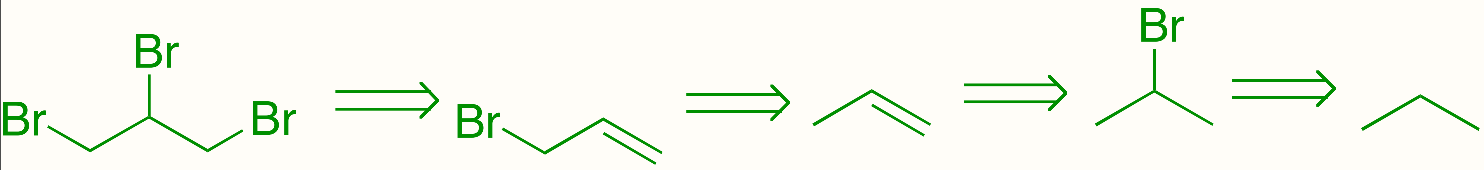
Professor Duncan Wardrop

April 1, 2010

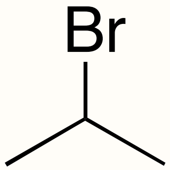
Self Test Question

Which starting material could *not* be used to prepare the tribromide below?





A



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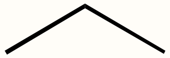
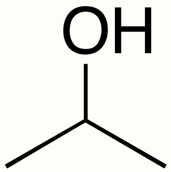
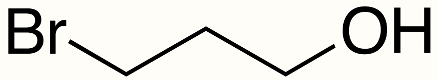


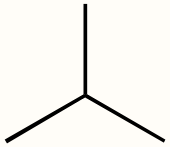
C



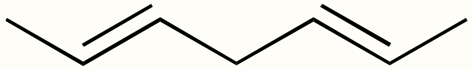
D



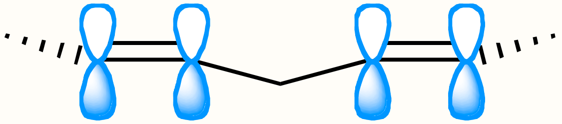
[✓ E]



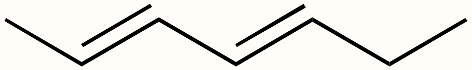
Classification of Dienes



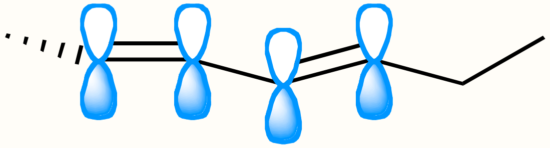
isolated diene



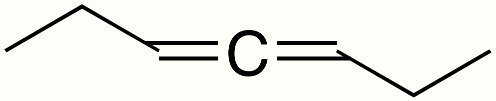
- two p-systems are not adjacent
- no overlap between 2 p-systems



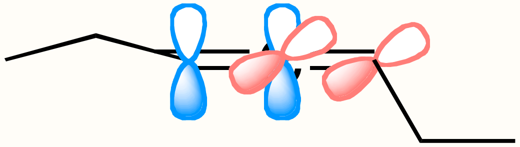
conjugated diene



- two p-systems are adjacent
- overlap exists between 2 p-systems

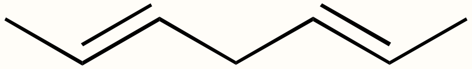


cummulated diene
(allene)



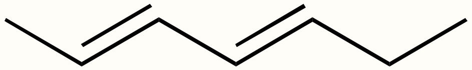
- central carbon atom is part of two p-systems
- central carbon = sp
- p orbitals for each p-system are perpendicular

Nomenclature



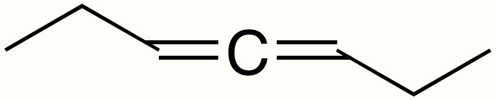
isolated diene

(2*E*, 5*E*)-2,5-heptadiene



conjugated diene

(2*E*, 4*E*)-2,4-heptadiene

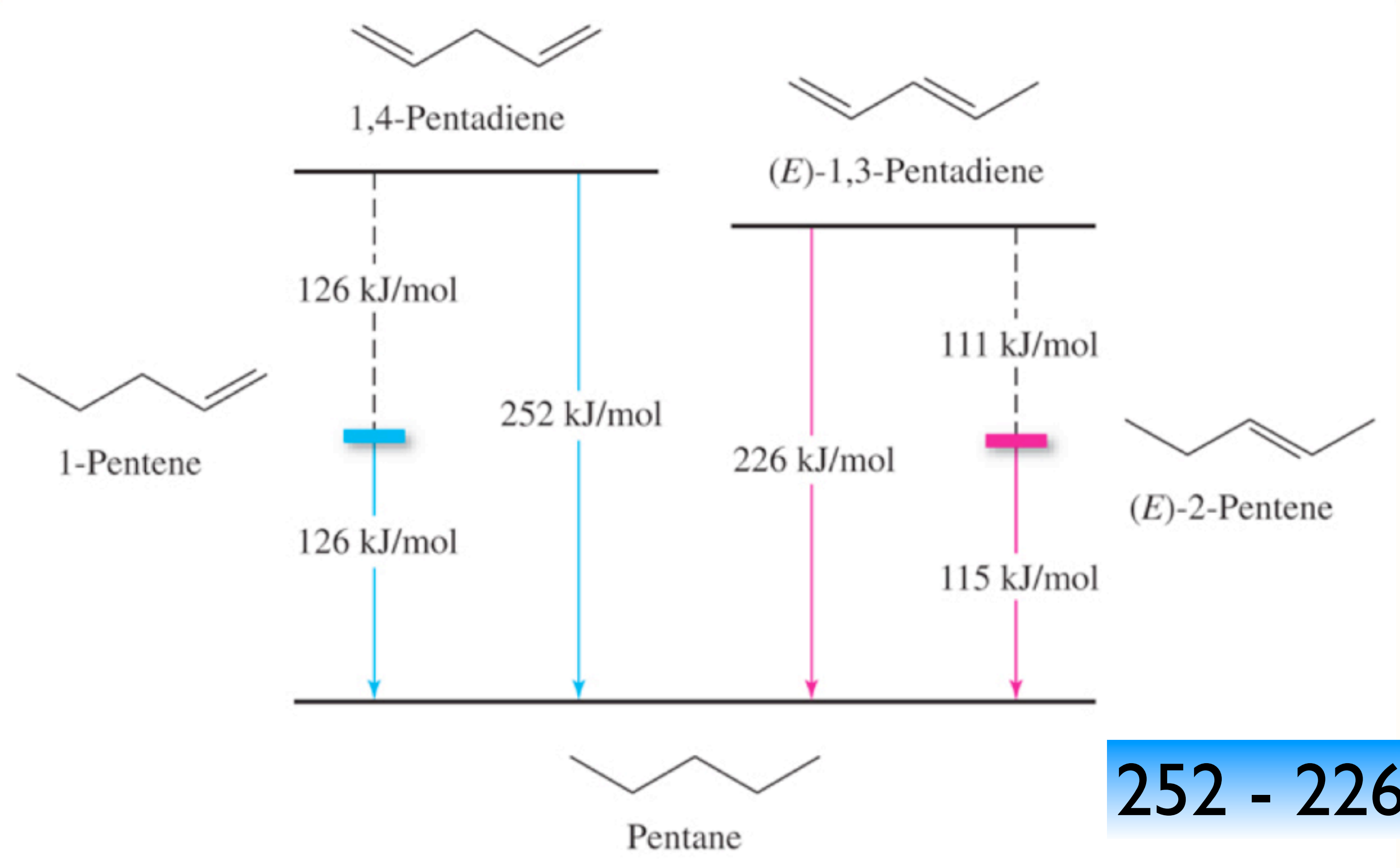


cummulated diene (allene)

3,4-heptadiene

Relative Stabilities of Dienes

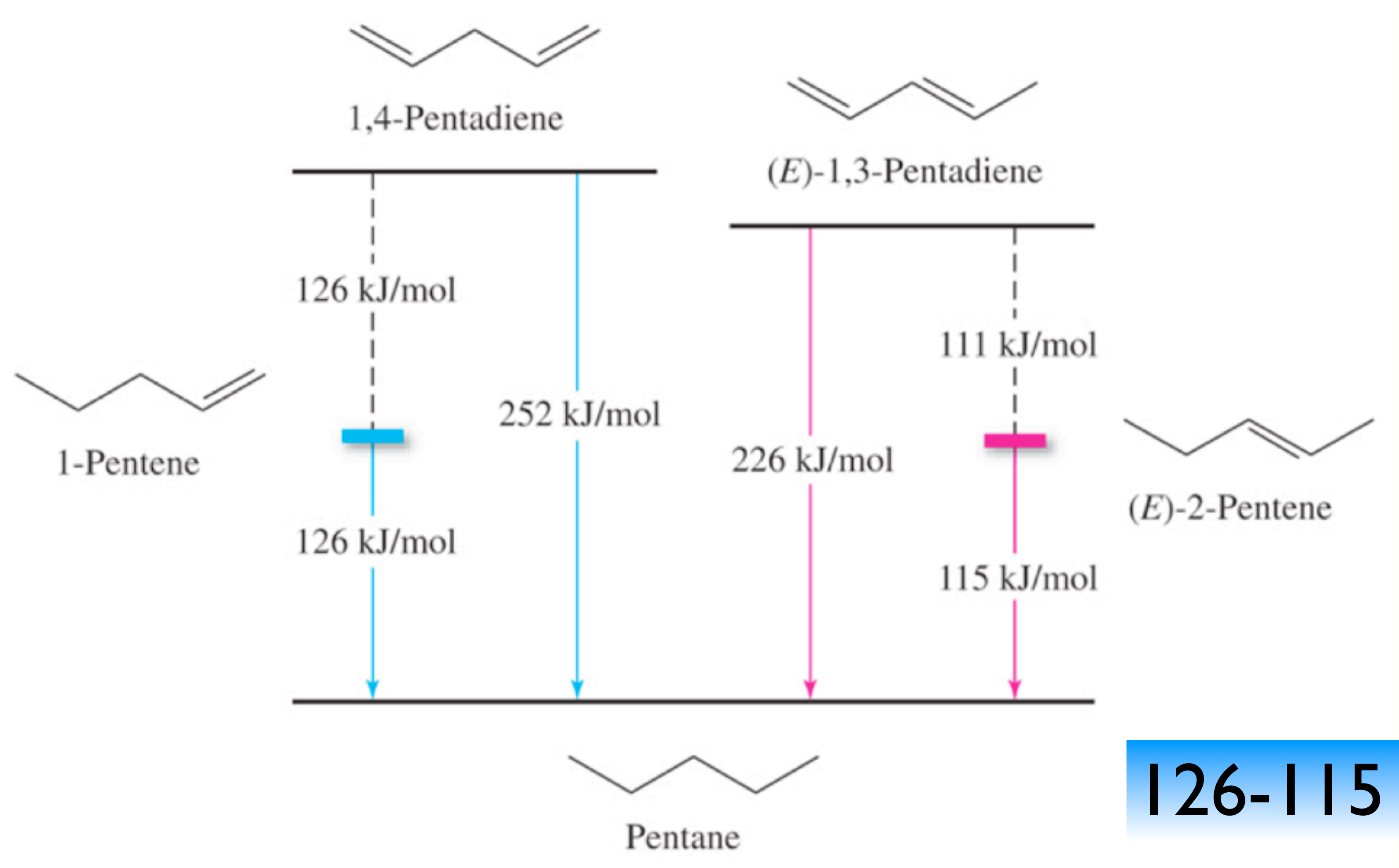
(*E*)-1,3-Pentadiene is 26 kJ/mol more stable than 1,4-pentadiene. Two reasons: more subst. & conjugation.



252 - 226 = 26

“Substitution” Energy

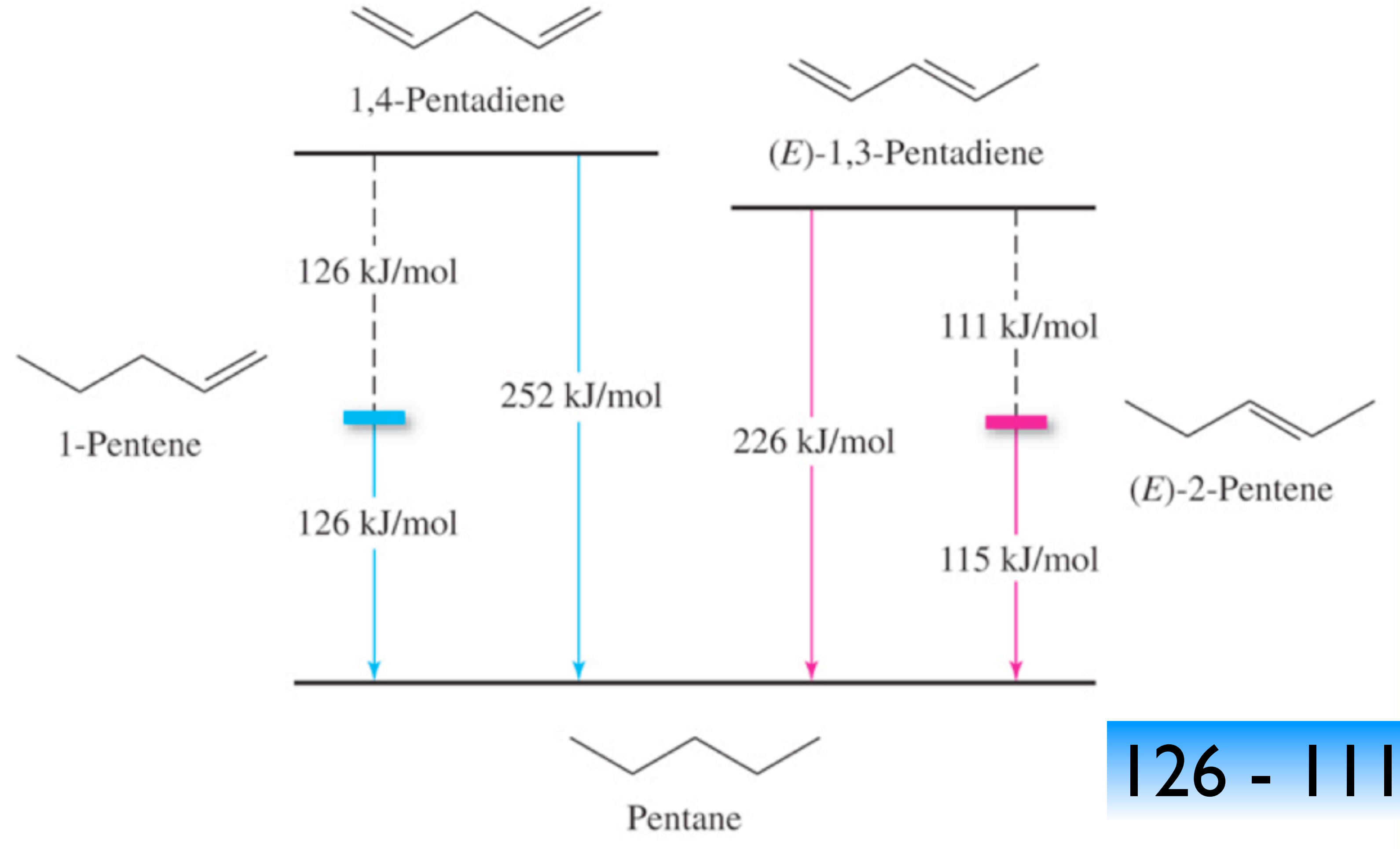
(*E*)-2-Pentene is disubstituted and is 11 kJ/mol more stable than 1-pentene, which is monosubstituted.



126-115 = 11

Delocalization Energy

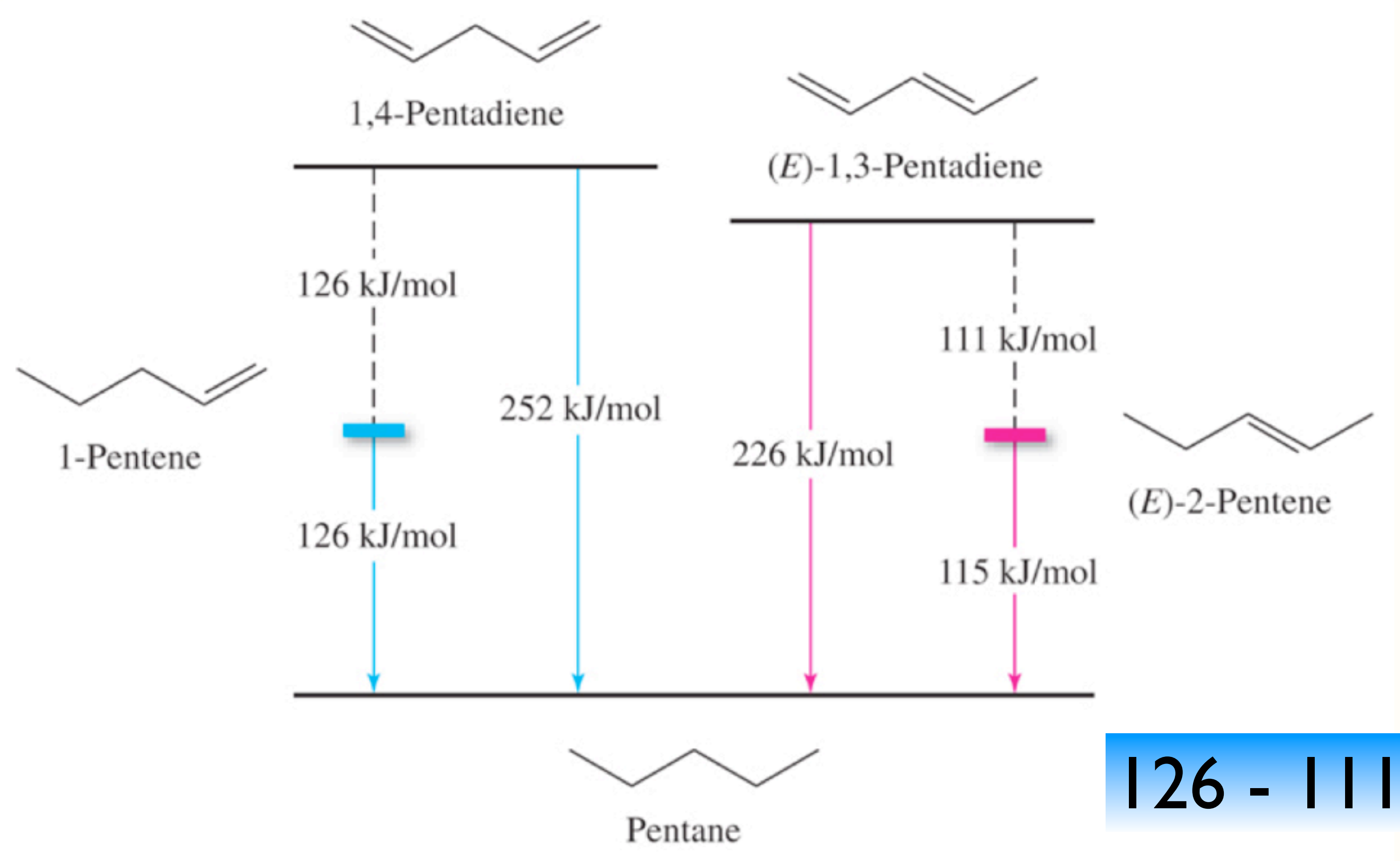
Upon hydrogenation of the terminal alkene, the conjugated double bond releases 15 kJ/mol **less** than non-conjugated



126 - 111 = 15

Delocalization Energy

Extra stability due to conjugation = conjugation energy or resonance energy or **delocalization energy**



126 - 111 = 15

Self Test Question

List the molecules below in order of *increasing* heat of hydrogenation. *Hint: some are trienes.*

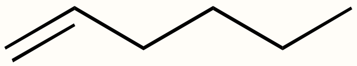
A. a,b,c,d,e

B. d,e,c,b,a

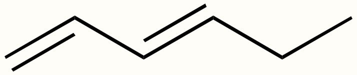
[✓ C.] a,c,b,e,d

D. a,b,c,e,d

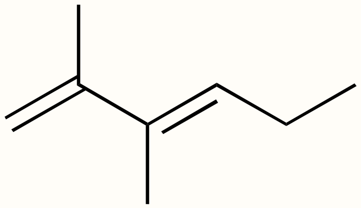
E. e,d,b,c,a



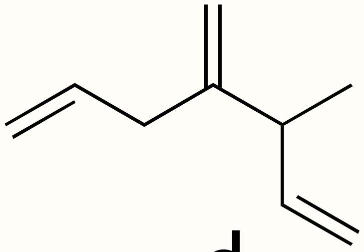
a



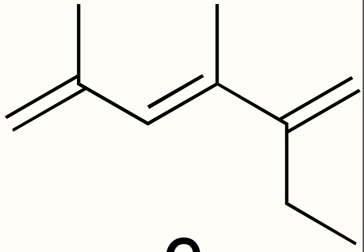
b



c

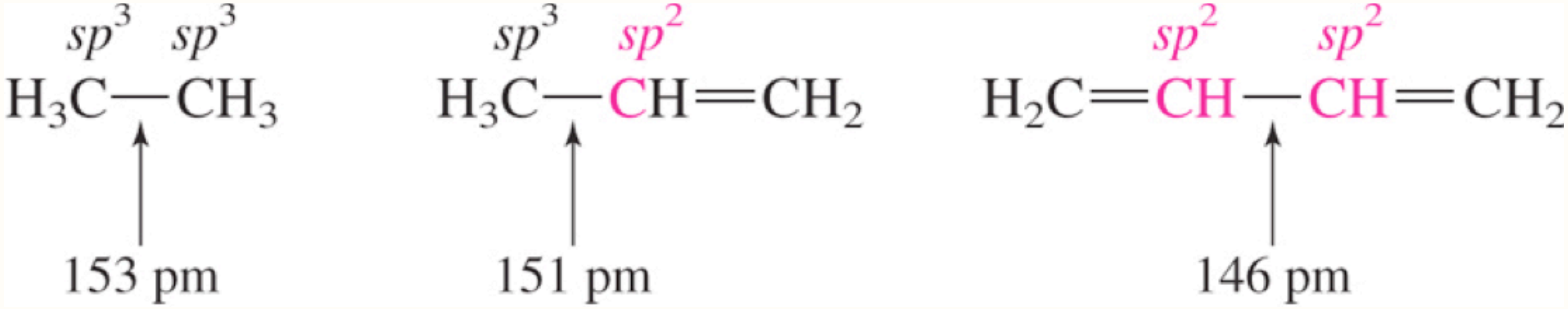


d



e

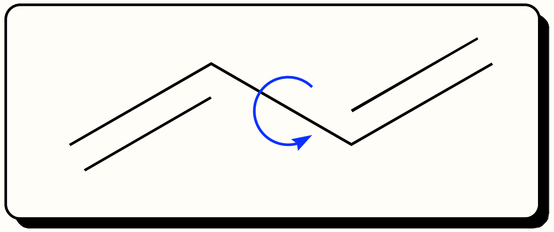
Bonding in Conjugated Dienes

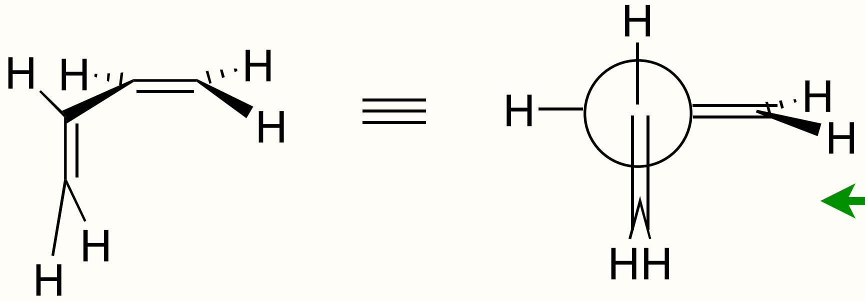


$$H_3\overset{sp^3}{C}\underset{\overset{\uparrow}{153\ \text{pm}}}{-}\overset{sp^3}{C}H_3 \qquad H_3\overset{sp^3}{C}\underset{\overset{\uparrow}{151\ \text{pm}}}{-}\overset{sp^2}{C}H=CH_2 \qquad H_2C=\overset{sp^2}{C}H\underset{\overset{\uparrow}{146\ \text{pm}}}{-}\overset{sp^2}{C}H=CH_2$$

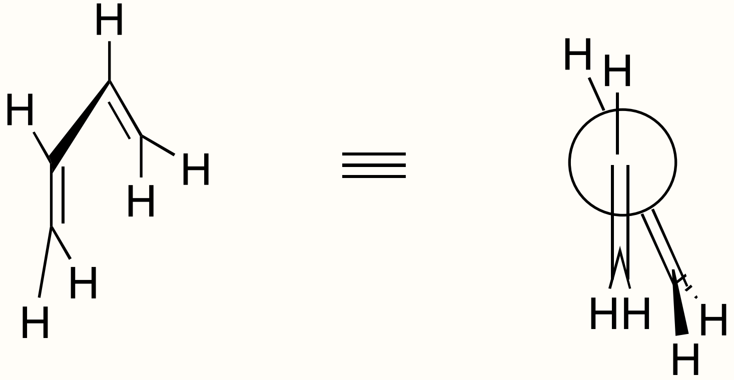
- single bonds between p-systems are stronger & shorter:
- increased s-character =
- increased attraction of electrons toward carbon nucleus =
- stronger C-C bonds =
- shorter bond lengths

Conformational Analysis of Dienes

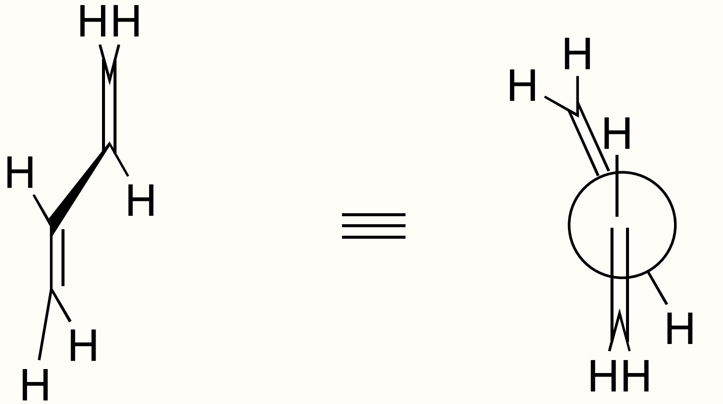




All groups are at 90° angles. Lowest NRG?

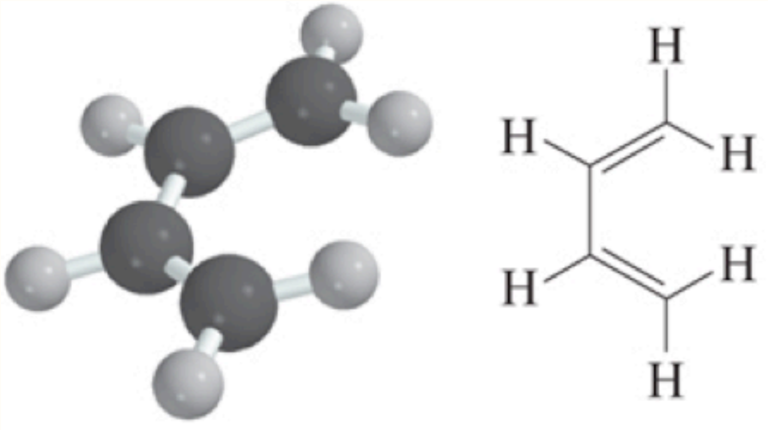


You might expect these conformations to be higher in energy since their are more eclipsing relationships.

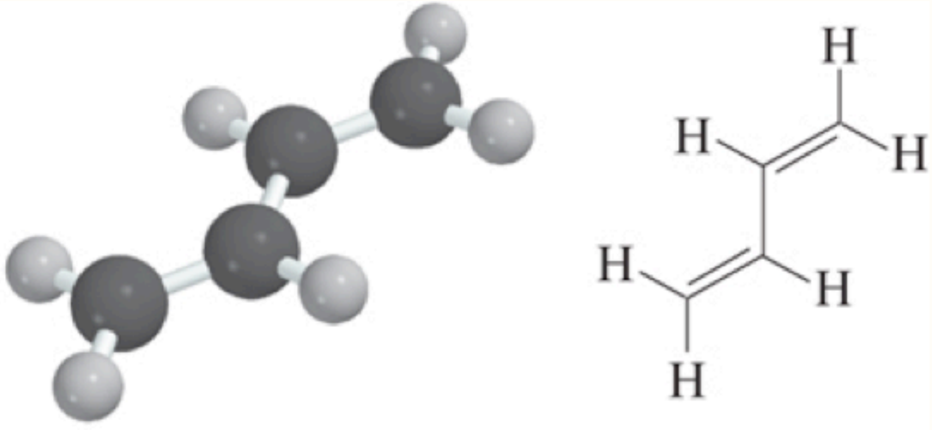


Conformations of Conjugated Dienes

Prefered conformations are *s*-Cis and *s*-Trans



s-Cis conformation of 1,3-butadiene



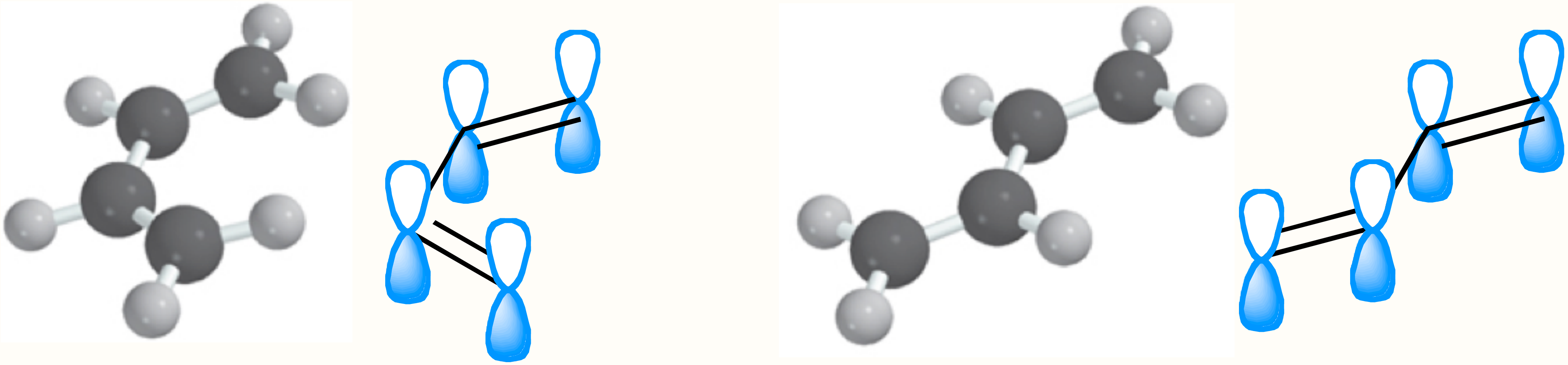
s-Trans conformation of 1,3-butadiene

↑ ↑

s = **s**ingle bond conformation between two alkenes

Conformations of Conjugated Dienes

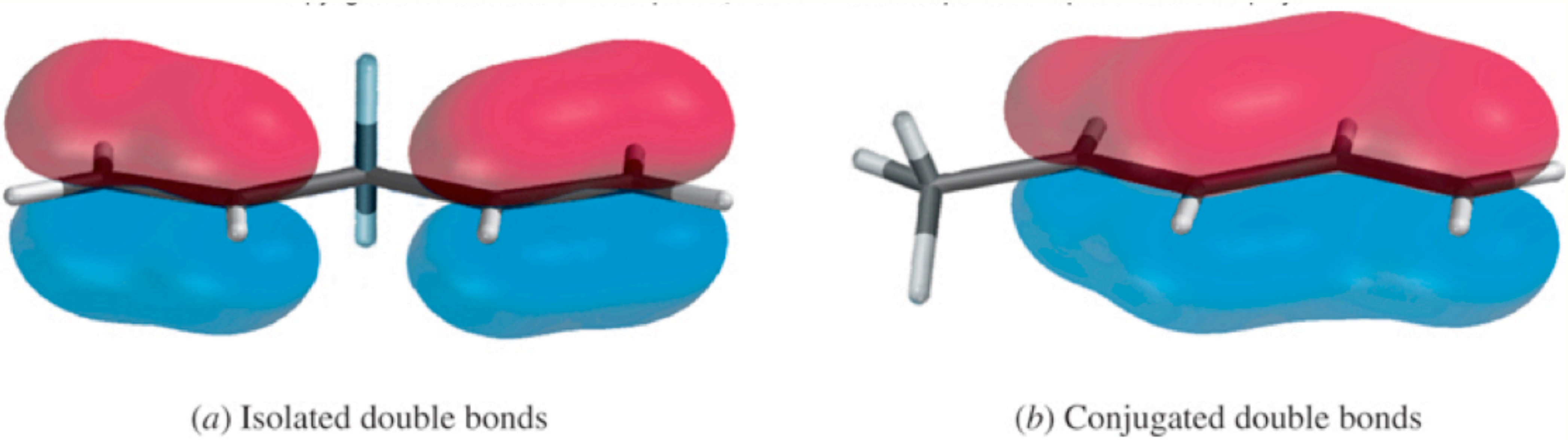
Prefered conformations are *s*-Cis and *s*-Trans



When two p-systems are co-planar they overlap and stabilize that conformation (delocalization energy)

Conformations of Conjugated Dienes

Prefered conformations are *s*-Cis and *s*-Trans

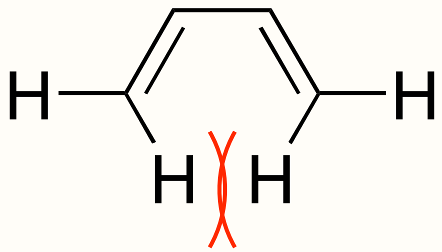

(*a*) Isolated double bonds

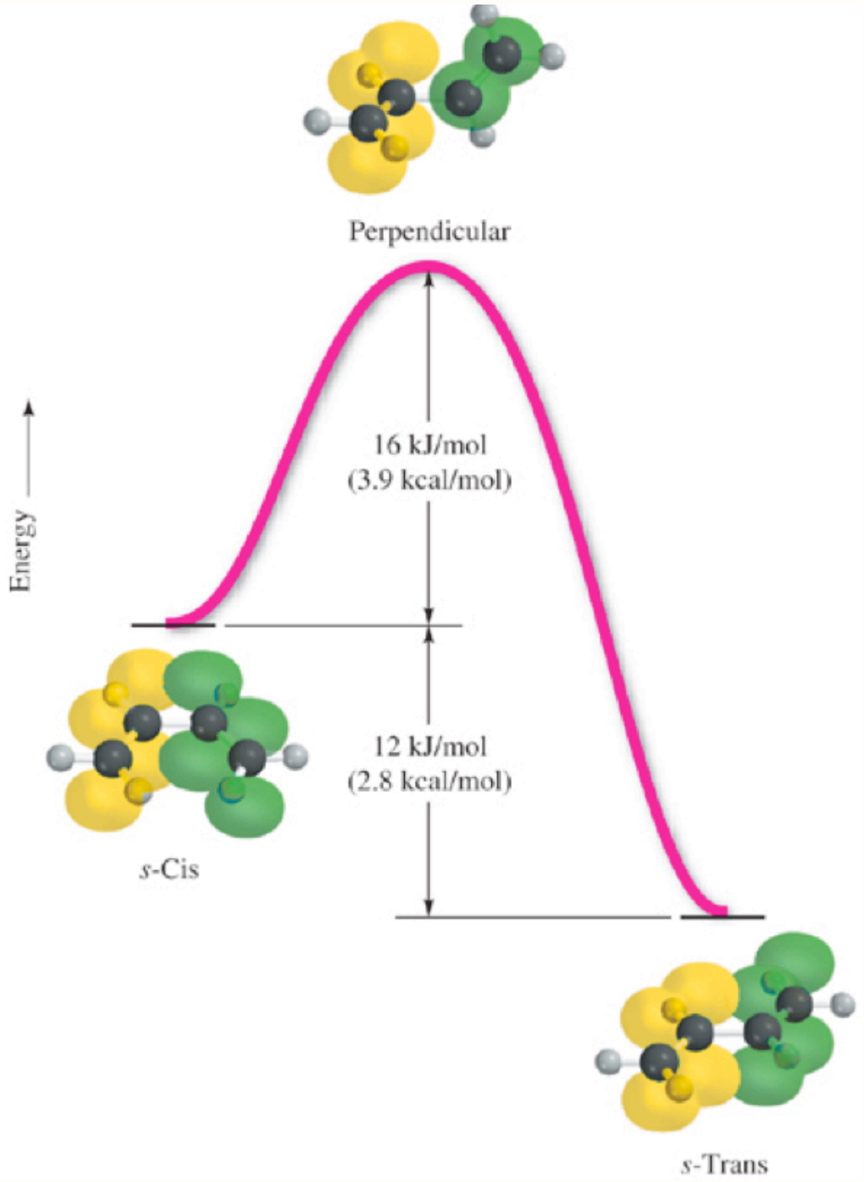
(*b*) Conjugated double bonds

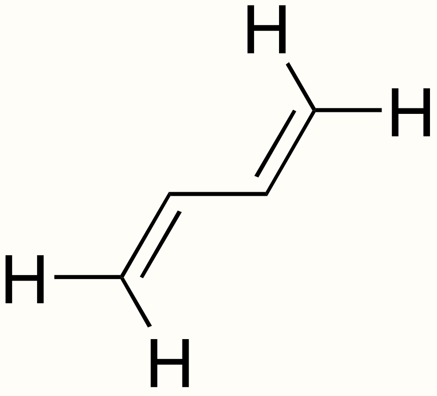
When two p-systems are co-planar they overlap and stabilize that conformation (delocalization energy)

s-Trans More Stable than *s*-Cis

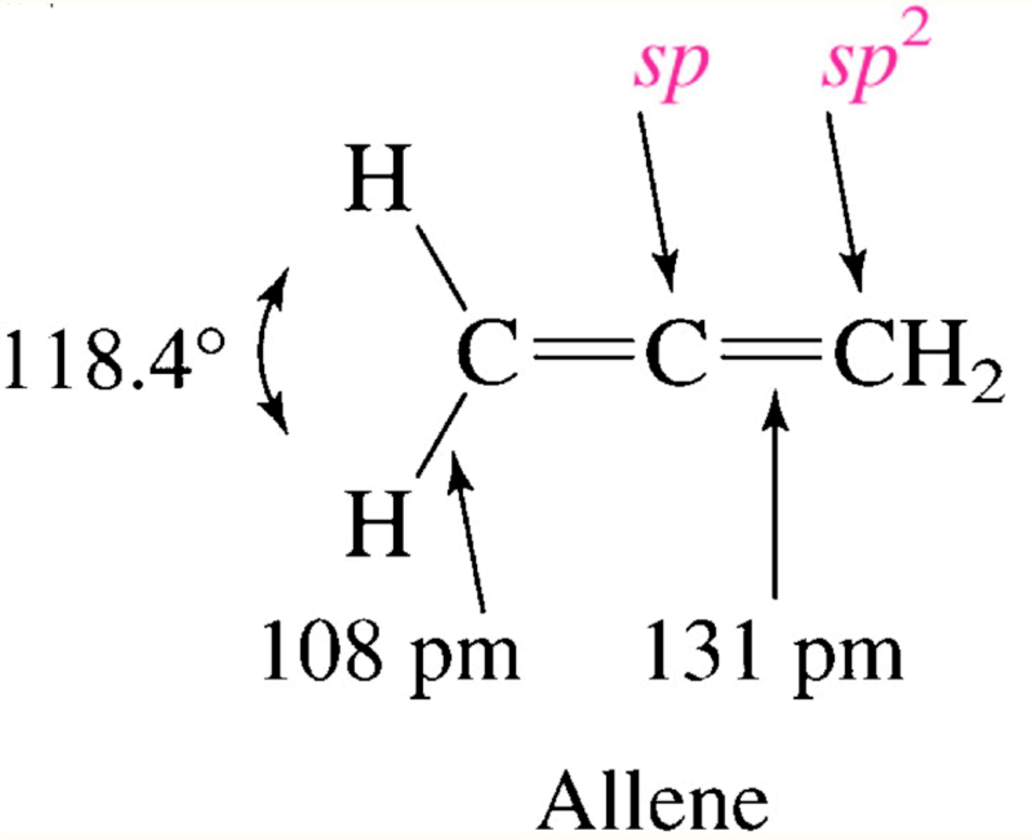
increased steric interactions in *s*-Cis







Bonding in Allenes

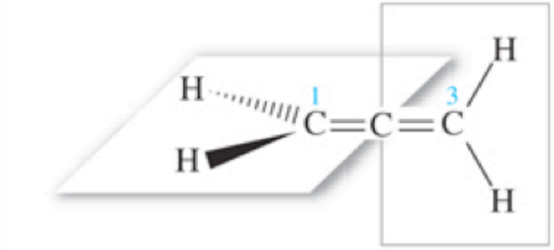


Allene

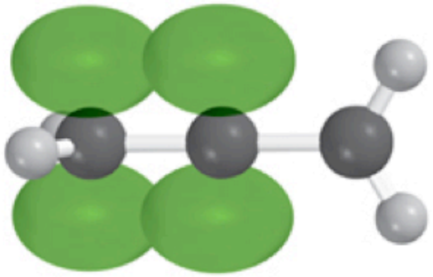
- central carbon atom is sp hybridized
- most s-character = stronger C-C bonds than even conjugated alkenes

Bonding in Allenes

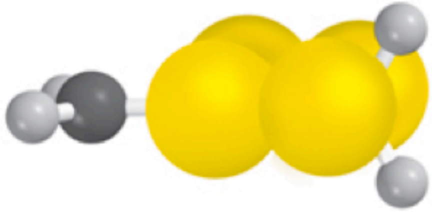
planes defined by H(C-1) and H(C-3) are perpendicular



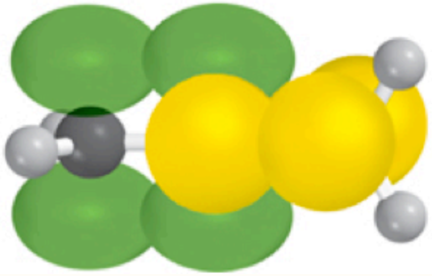
p-orbital of C-1 and *p*-orbital of C-2 overlap to form Π-bond



p-orbital of C-2 and *p*-orbital of C-3 overlap to form 2nd Π-bond



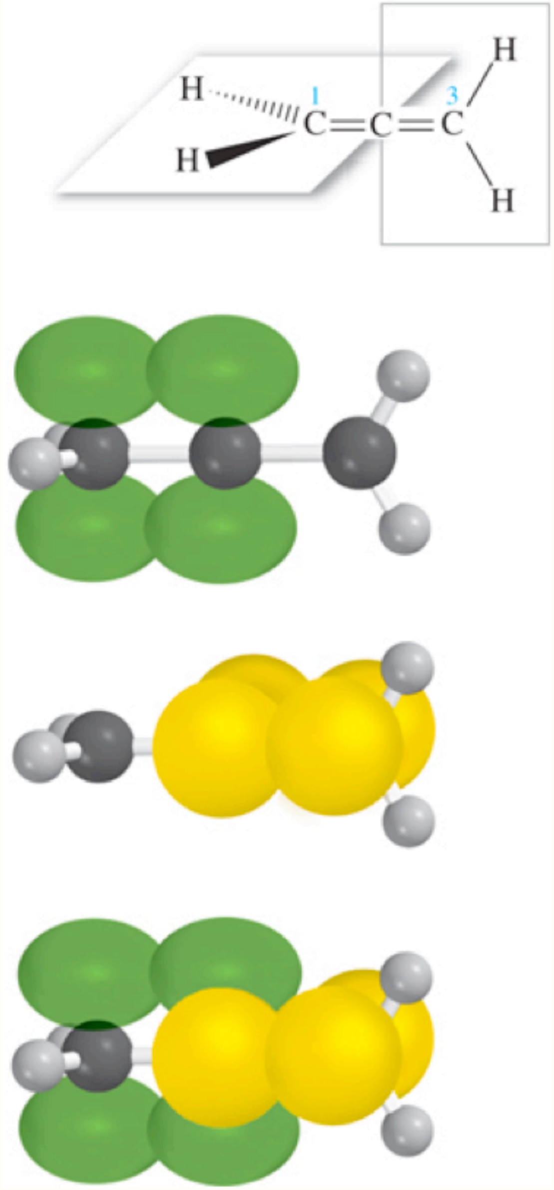
allene is nonplanar; two Π-bonds are perpendicular to each other



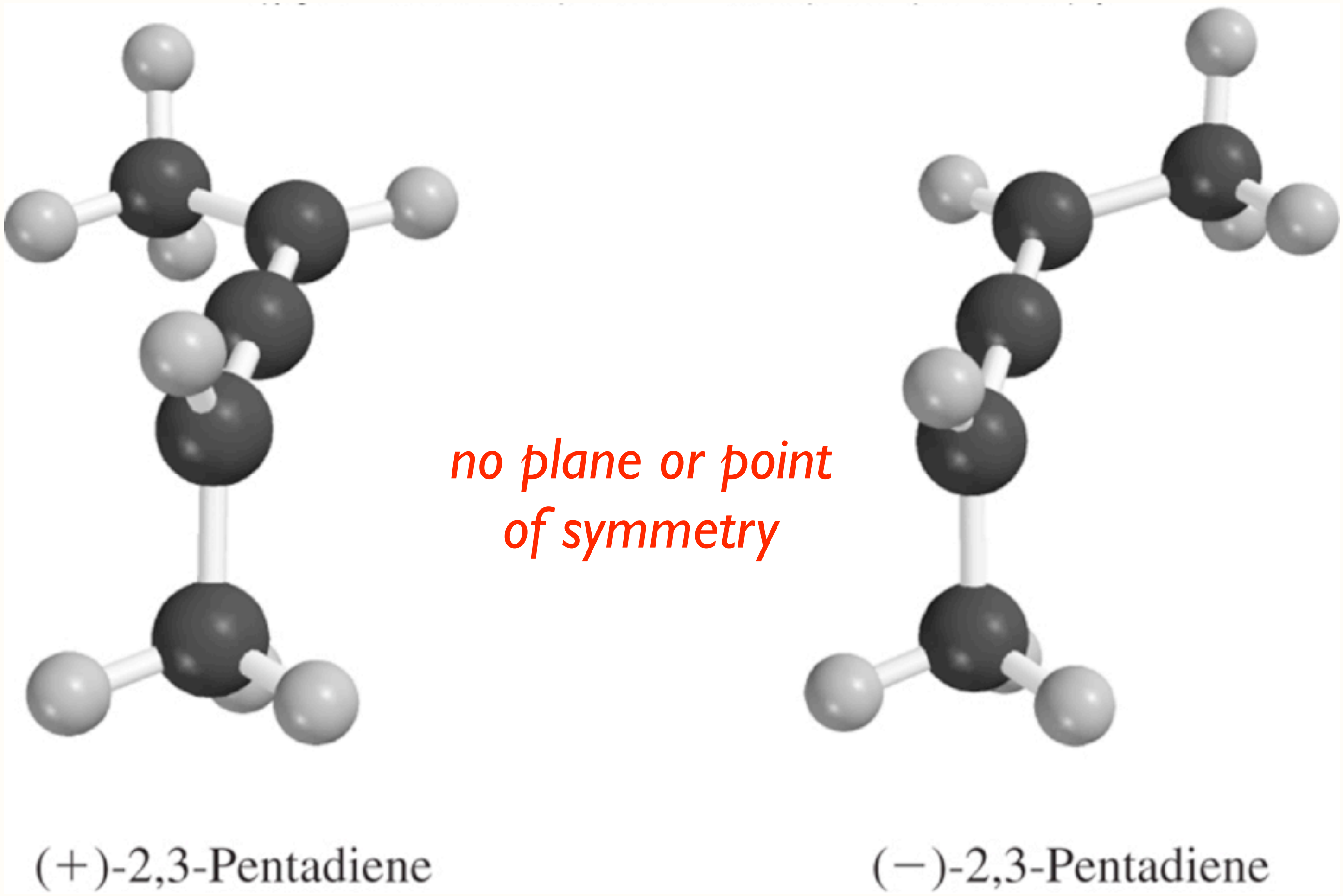
Bonding in Allenes

Q: Are allenes stabilized by delocalization energy?

A: No. π-systems are orthogonal/perpendicular. No overlap, and thus delocalization, is possible.



Allenes Can Be Chiral


no plane or point of symmetry

(+)-2,3-Pentadiene

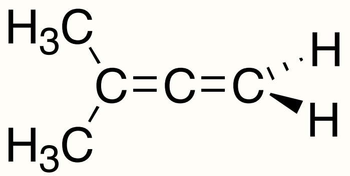
(−)-2,3-Pentadiene

These two allenes are enantiomers: non superimposible mirror images

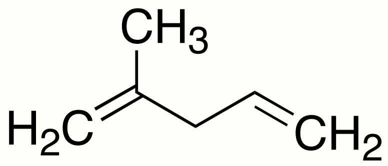
Self Test Question

Which of the following dienes is chiral?

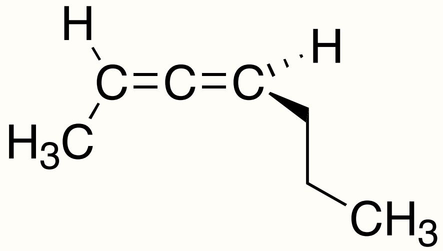
A. 2-methyl-2,3-butadiene



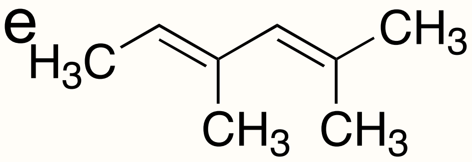
B. 2-methyl-1,4-pentadiene



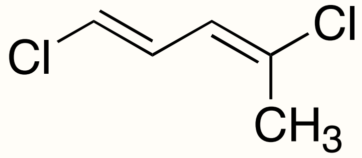
[✓ C.] 2,3-heptadiene



D. 2,4-dimethyl-2,4-hexadiene



E. 1,4-dichloro-1,3-pentadiene



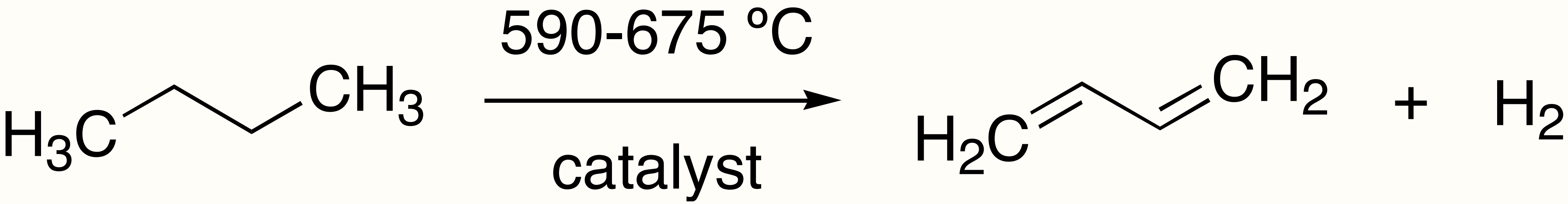
Chapter 10

Preparation & Reactions of Dienes

Sections: 10.12-10.15

Preparation of Dienes

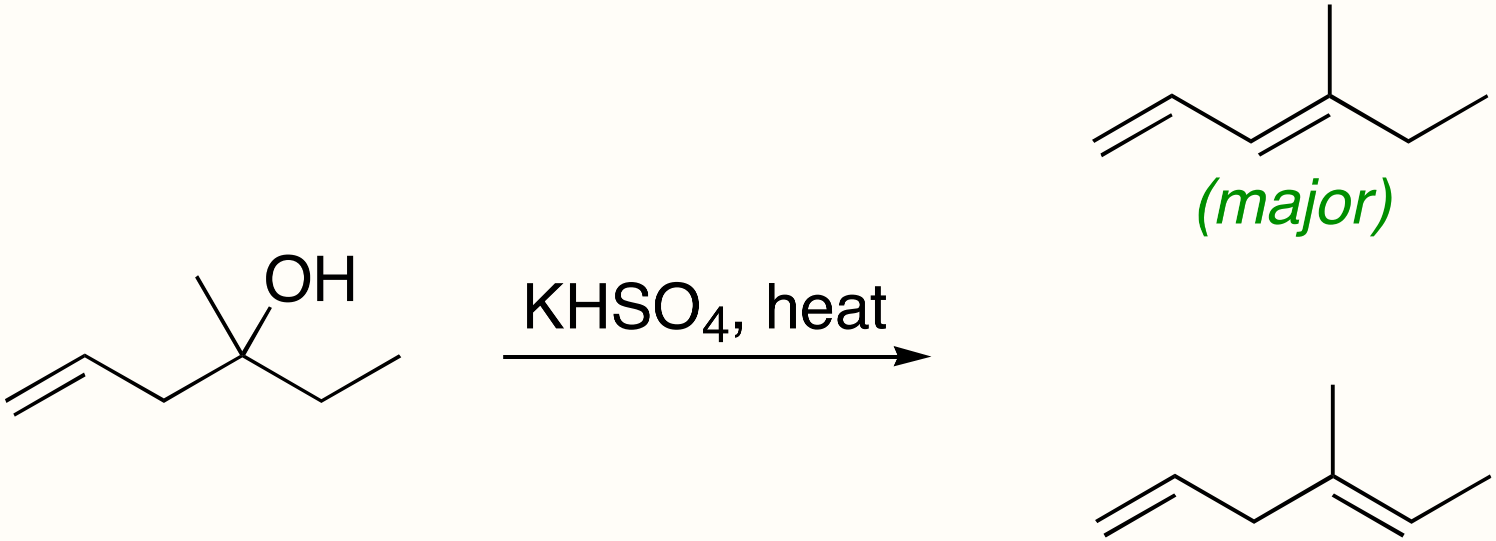
Dehydrogenation



This is an industrial process that works only when one possible diene can be obtained. Generally, it should not be used in the laboratory (synthesis questions).

Preparation of Dienes

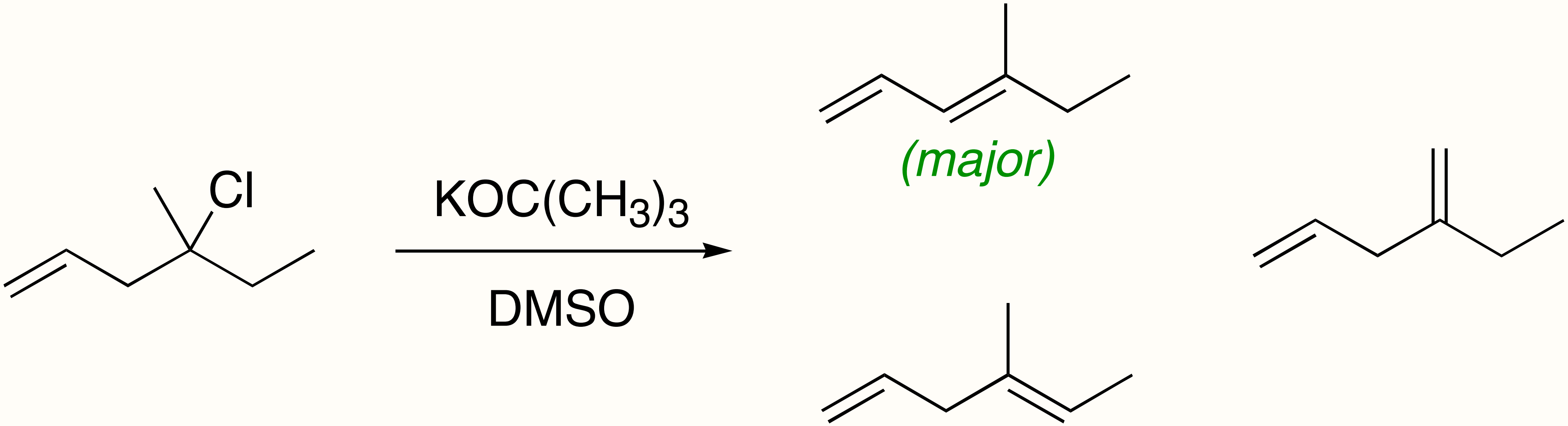
Dehydration



Dehydration is <u>regioselective</u>. The transition state leading to conjugated alkenes is lowest = fastest process.

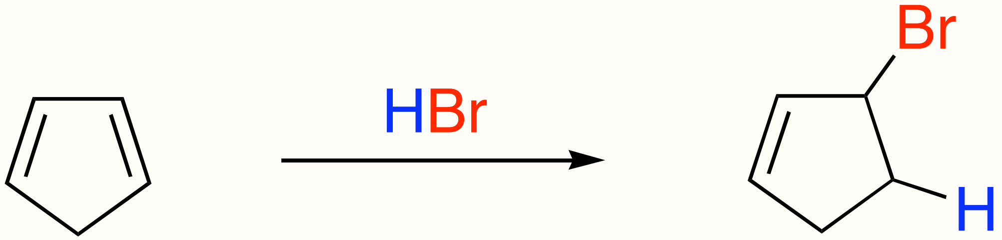
Preparation of Dienes

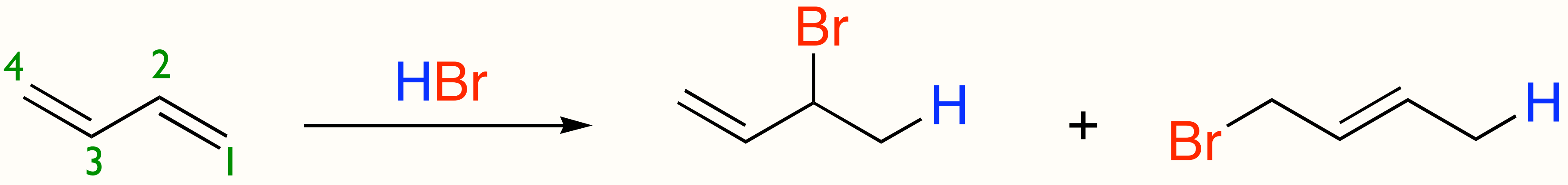
Dehydrohalogenation



Dehydrohalogenation is also regioselective. The transition state leading to conjugated alkenes is lowest = fastest process.

Addition of Hydrogen Halides to Conjugated Dienes





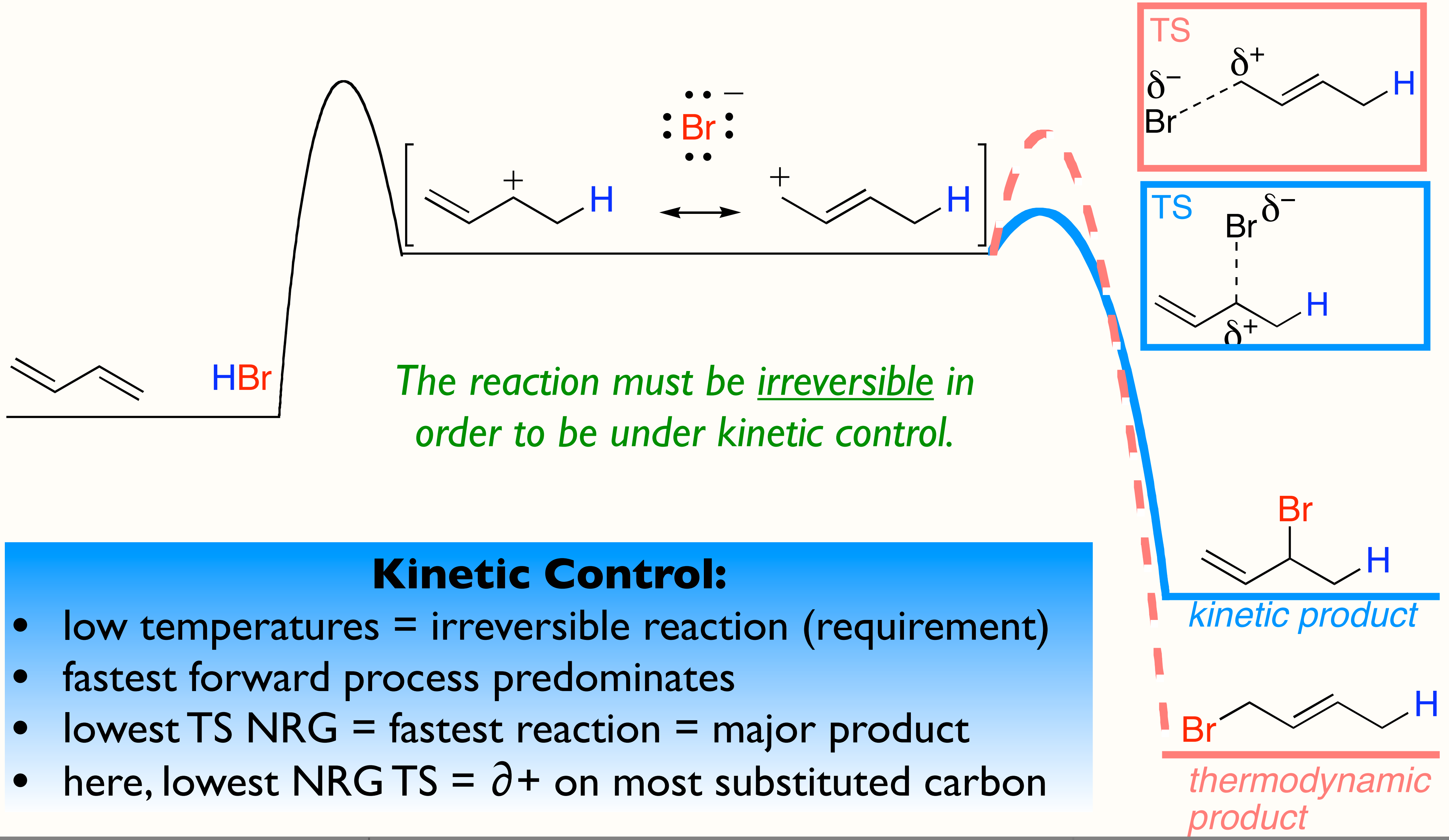
1,2-Addition Product (direct addition)

1,4-Addition Product (conjugate addition)

Kinetic product: major product at low temperature

Thermodynamic product: major product at high temp.

Control of HX Addition to Conjugated Dienes

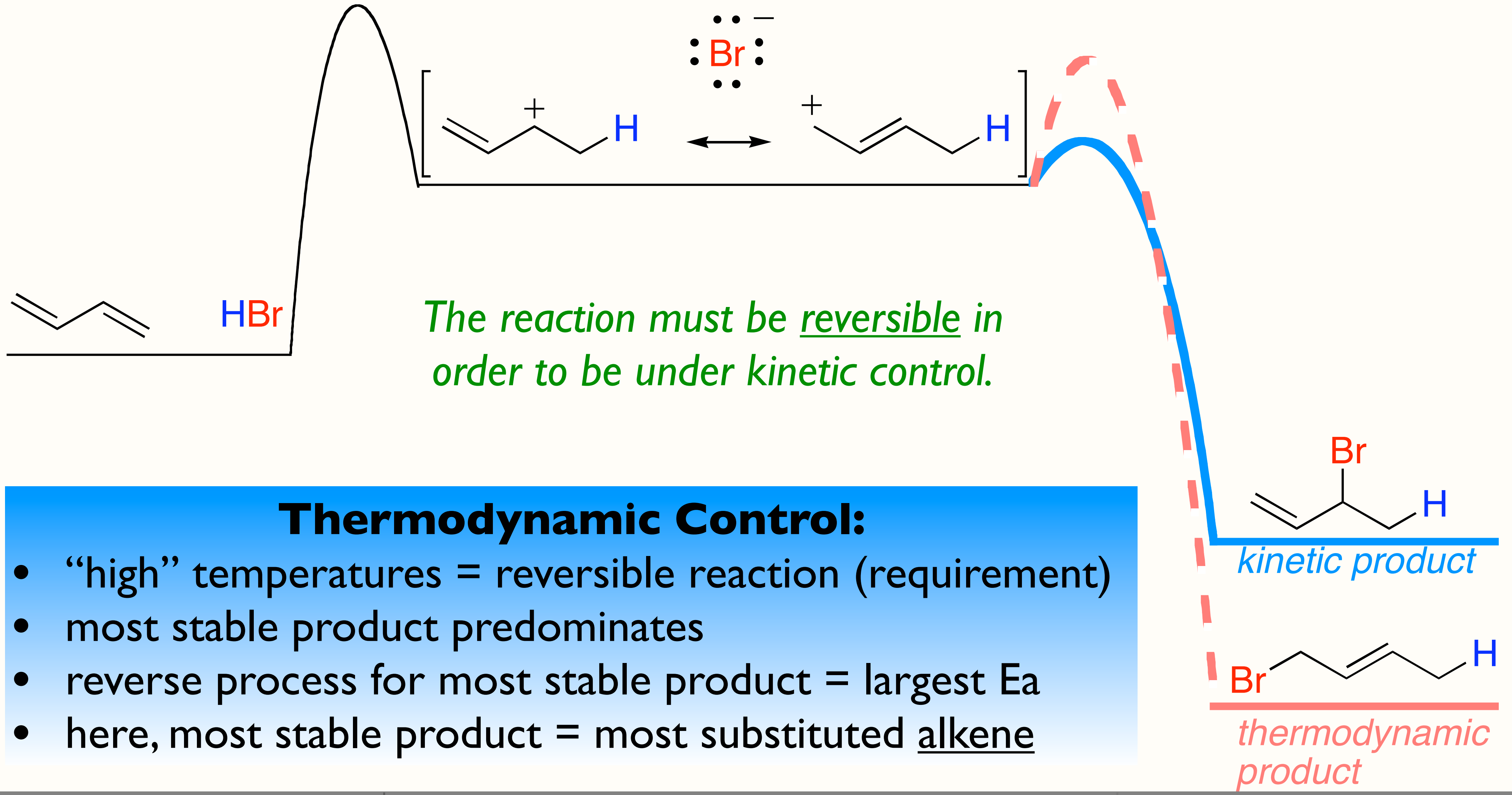


The reaction must be irreversible in order to be under kinetic control.

Kinetic Control:

- low temperatures = irreversible reaction (requirement)
- fastest forward process predominates
- lowest TS NRG = fastest reaction = major product
- here, lowest NRG TS = ∂+ on most substituted carbon

Control of HX Addition to Conjugated Dienes

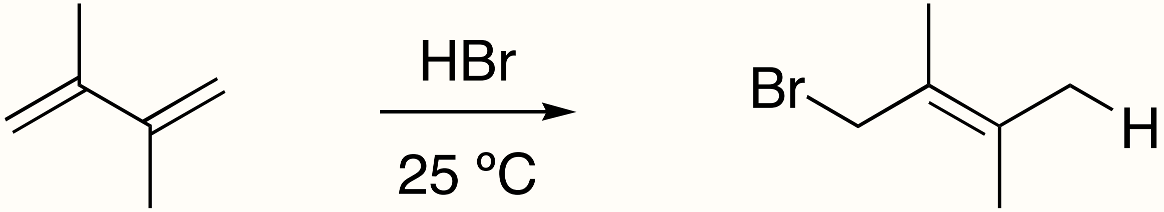


The reaction must be <u>reversible</u> in order to be under kinetic control.

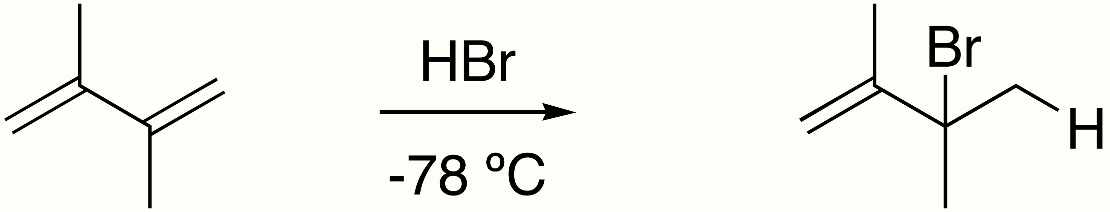
Thermodynamic Control:

- "high" temperatures = reversible reaction (requirement)
- most stable product predominates
- reverse process for most stable product = largest Ea
- here, most stable product = most substituted <u>alkene</u>

Conditions of Kinetic and Thermodynamic Control



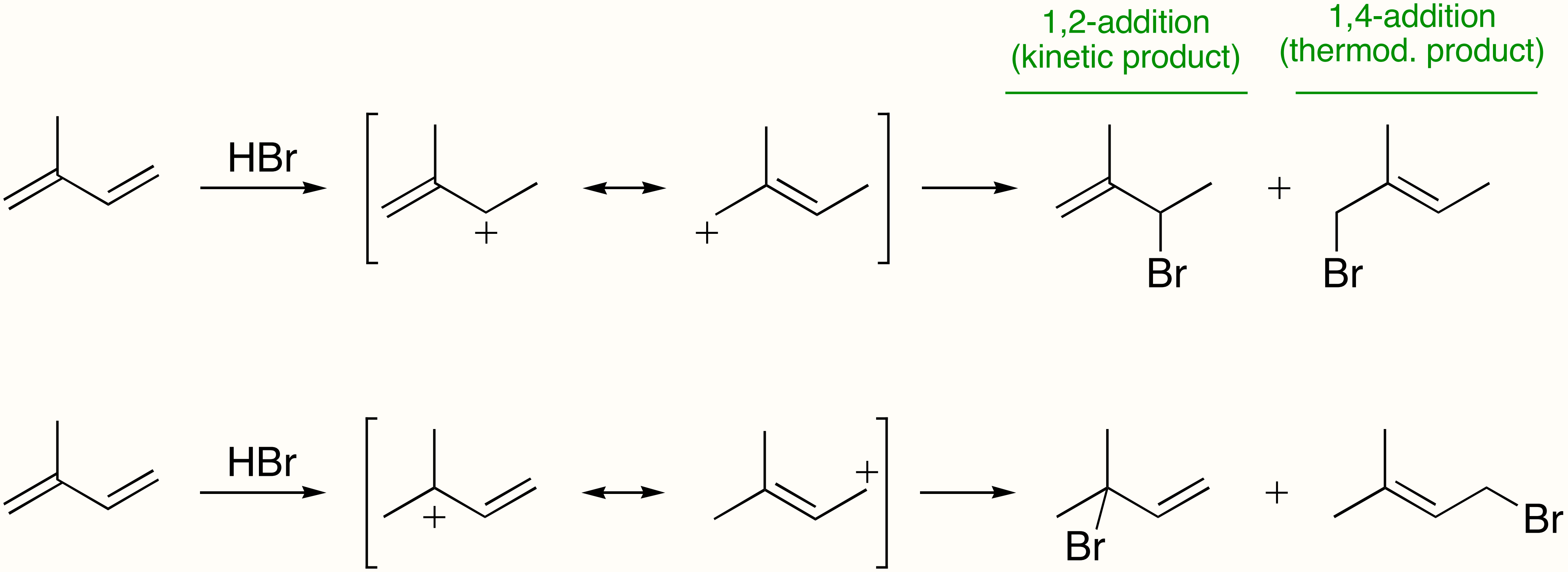
1,4-addition
(thermodynamic product)



1,2-addition
(kinetic product)

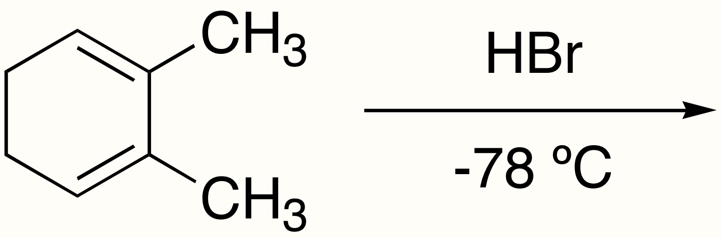
Addition of HX to Conjugated Dienes

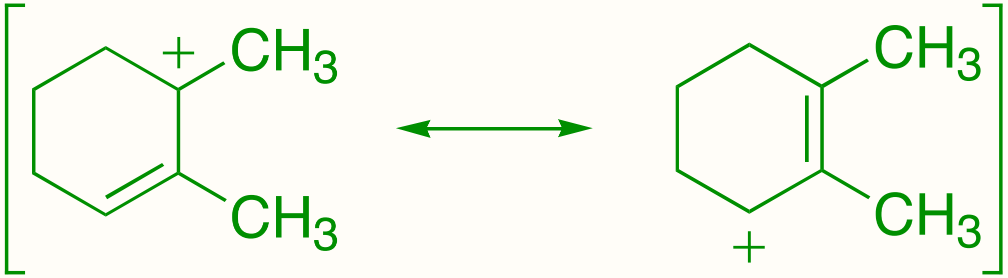
Addition of HX to conjugated dienes is only useful in synthesis when there is only one carbocation intermediate; each resonance form does not count separately



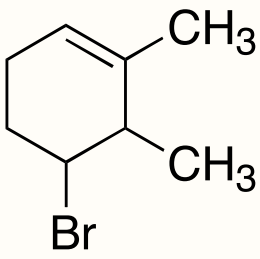
Self Test Question

What is the *kinetic product* for HBr addition to the conjugated diene below?





A



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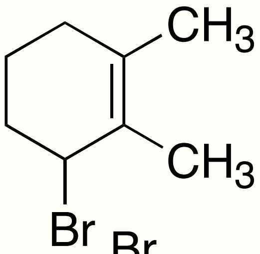
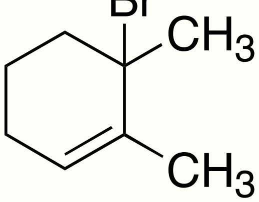
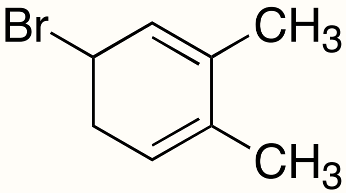


[✓ C]



D



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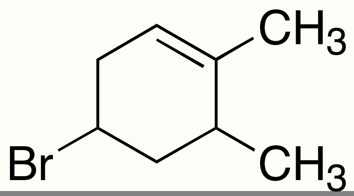
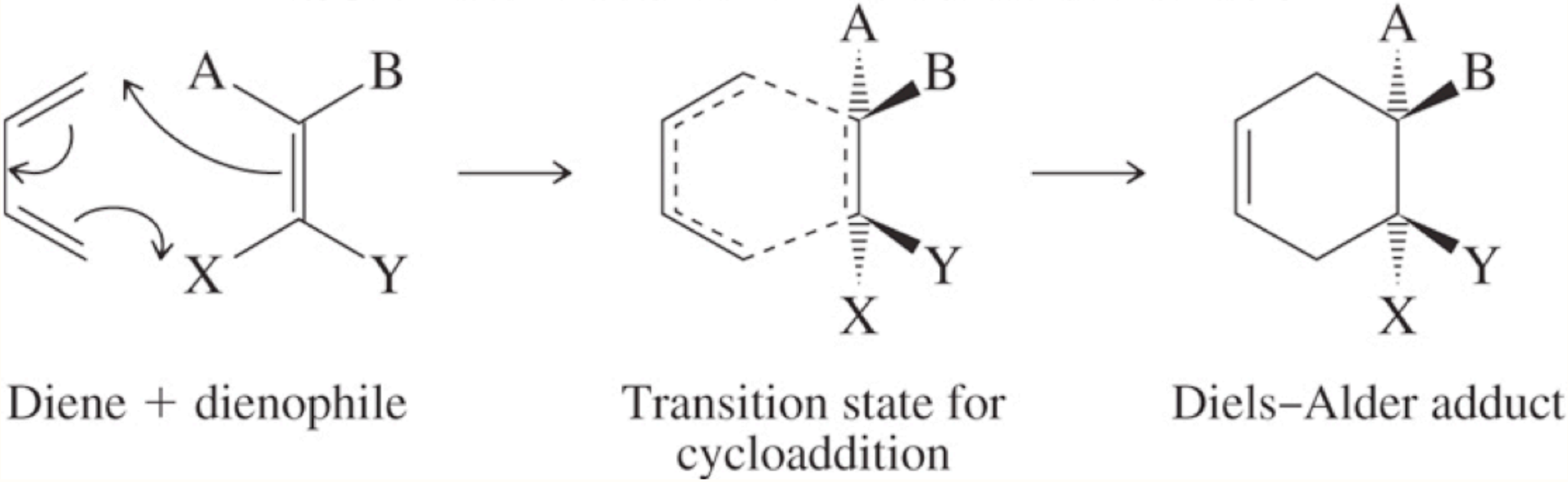


Diels-Alder Reaction

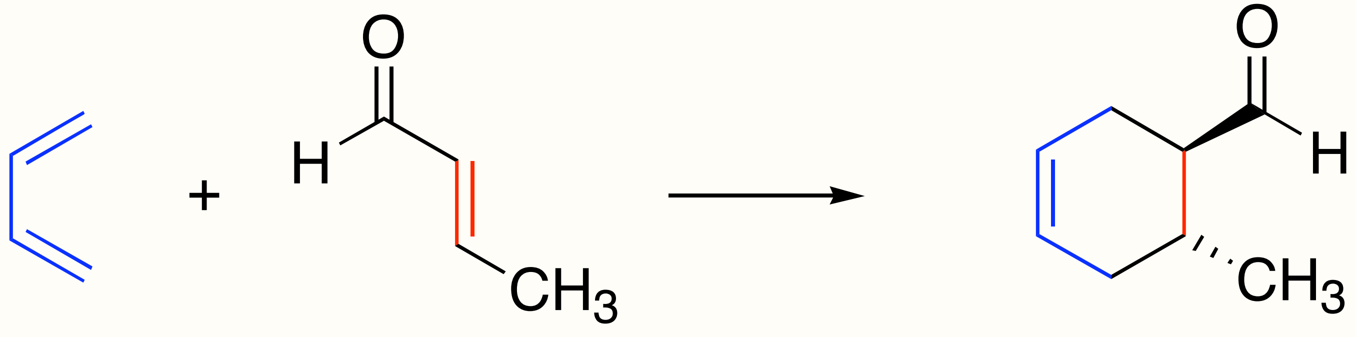


Terminology

- **cycloaddition:** forming a six-membered ring
- **dienophile:** typically an isolated alkene; "lover of" dienes (conjugated)
- **pericyclic reaction:** concerted rxn where transition state is cyclic (ring)
- **Diels-Alder adduct:** potentially any molecule with a cyclohexene ring

Diels-Alder Reaction

Diels-Alder reaction is **stereospecific** (the stereoisomeric product formed depends on the stereoisomer of the reactant).



diene dienophile Diels-Alder adduct

Substituents that are *trans* on the dienophile are also *trans* in the Diels-Alder adduct.

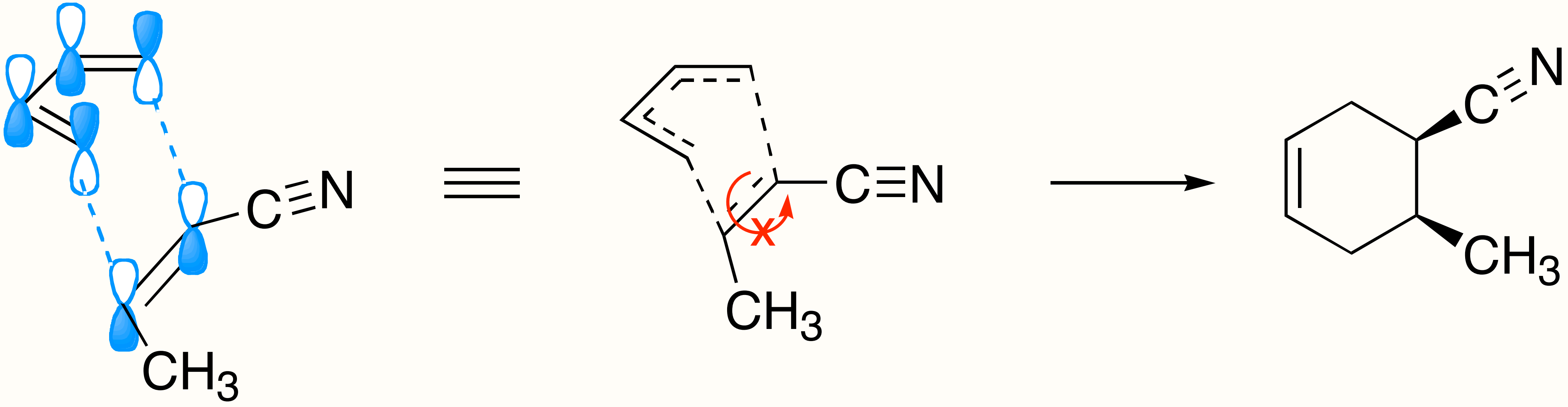
Diels-Alder Reaction

Diels-Alder reaction is **stereospecific** (the stereoisomeric product formed depends on the stereoisomer of the reactant).

diene dienophile Diels-Alder adduct

Substituents that are *cis* on the dienophile are also *cis* in the Diels-Alder adduct.

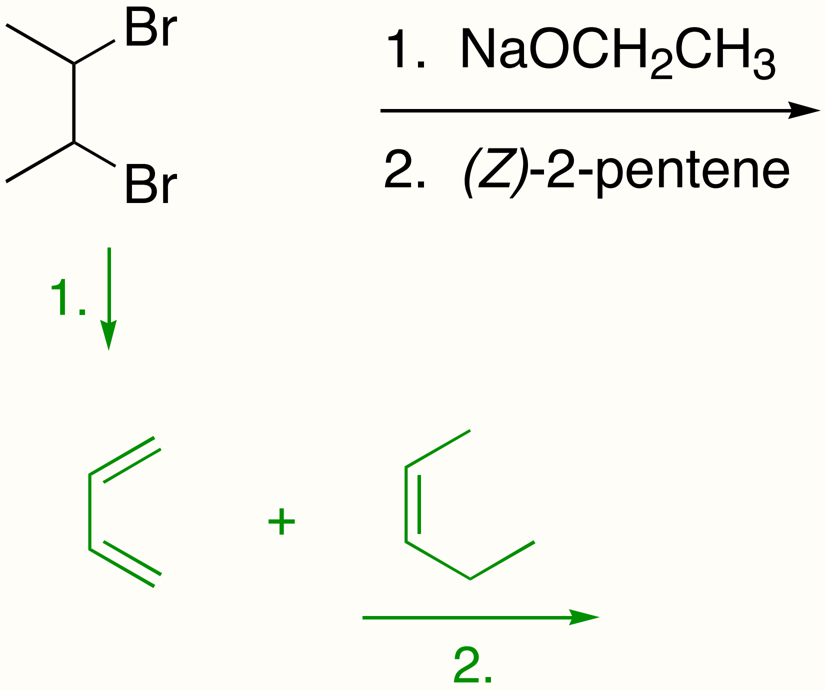
Diels-Alder Reaction



- to form new bonds, p-orbitals of diene overlap with p-orbitals of dienophile
- both bonds are being formed at the same time
- cannot rotate around dienophile bond =
- relationships of groups don't change

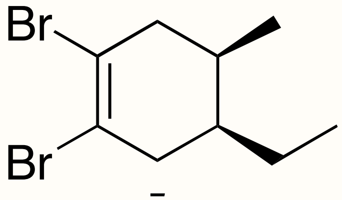
Self Test Question

Predict the product.

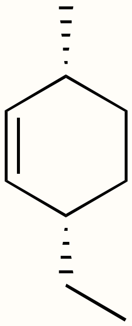

1. NaOCH$_2$CH$_3$

2. (*Z*)-2-pentene

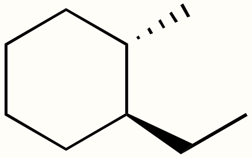
A



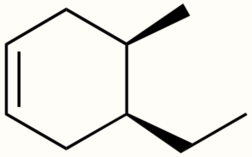
B



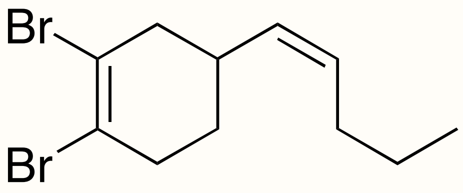
C



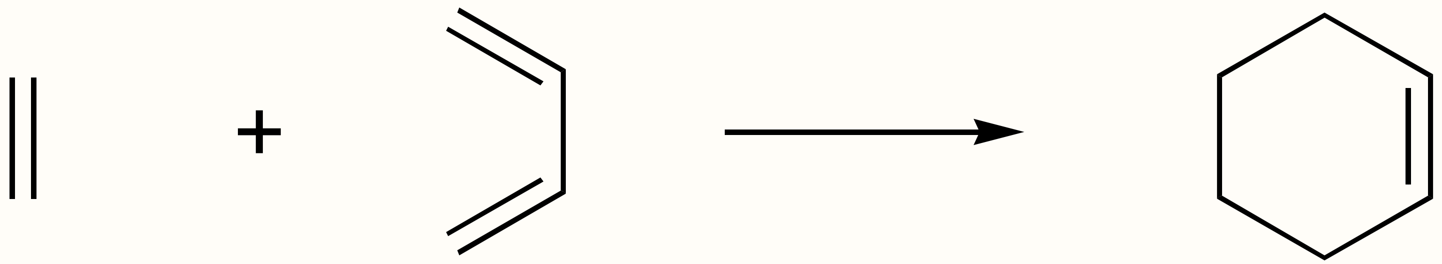
[✓ D]



E

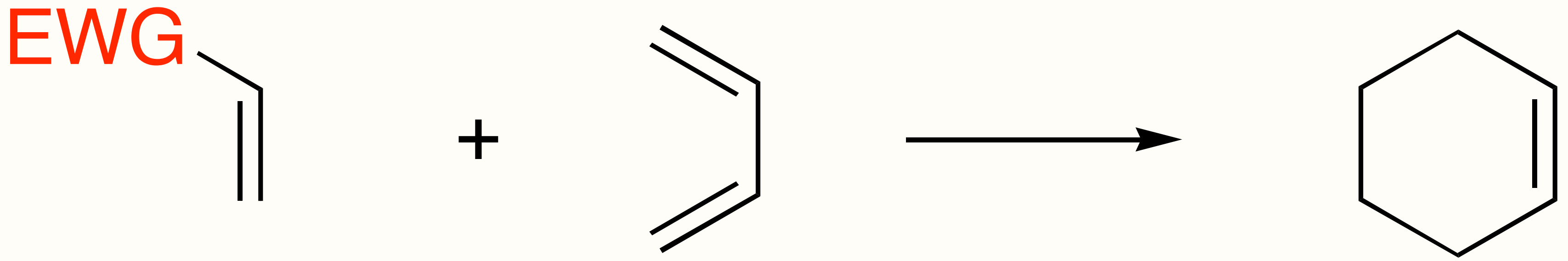


Reactivity of Diels Alder



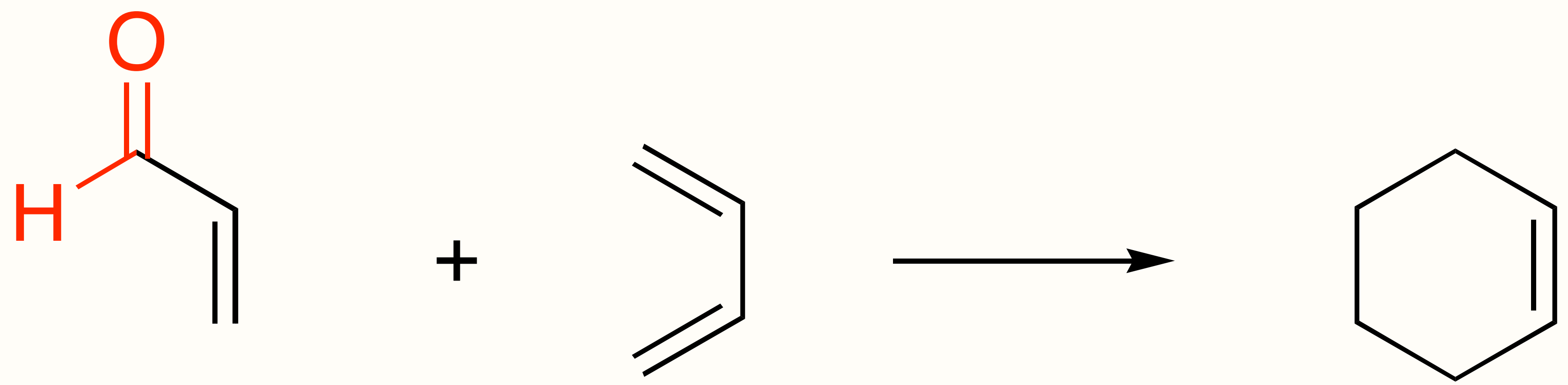
Ethylene and 1,3-butadiene are unreactive.
In other words, they react very slowly.

Reactivity of Diels Alder



Electron withdrawing groups (EWG) increase the reactivity of the dienophile = faster reaction

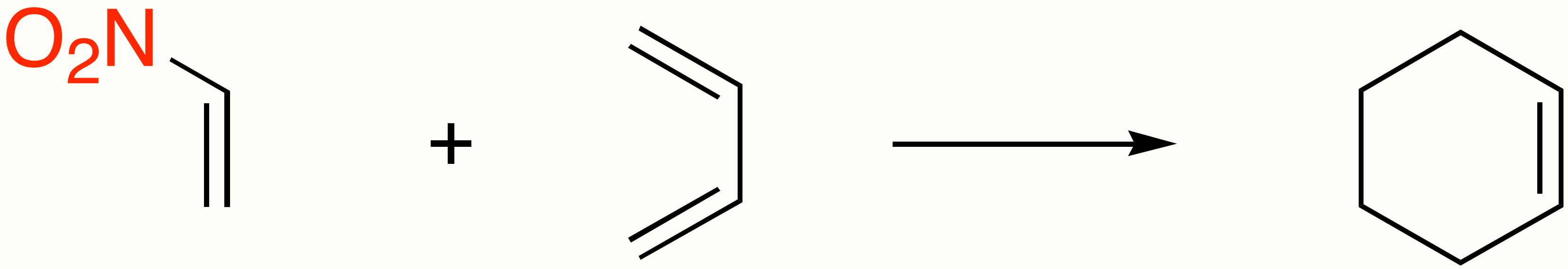
Reactivity of Diels Alder



carbonyl groups

Electron withdrawing groups (EWG) increase the reactivity of the dienophile = faster reaction

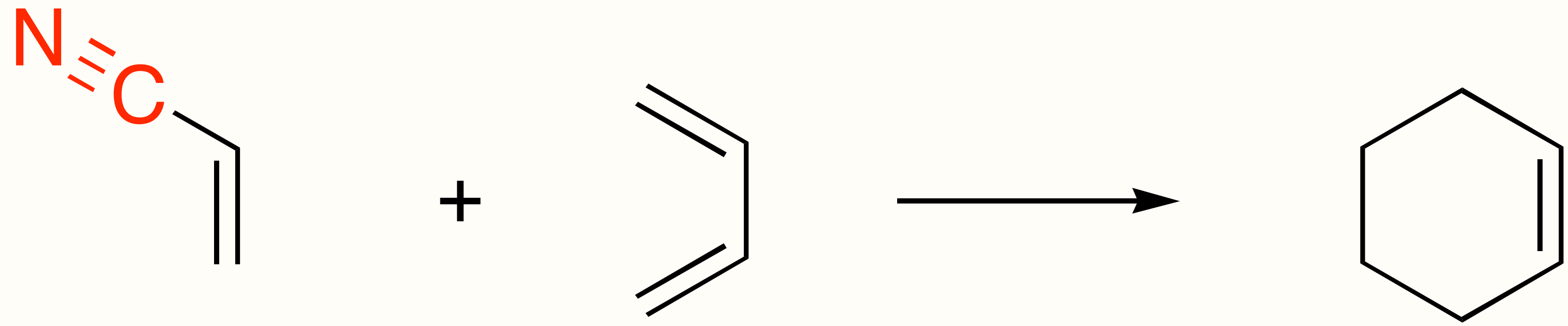
Reactivity of Diels Alder



nitro
group

Electron withdrawing groups (EWG) increase the reactivity of the dienophile = faster reaction

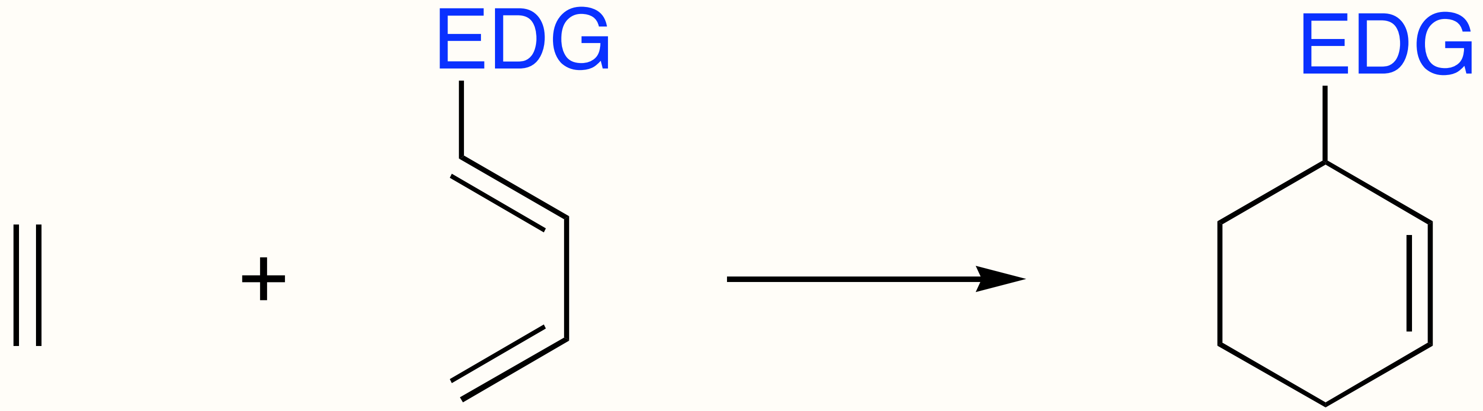
Reactivity of Diels Alder



nitrile (cyano) group

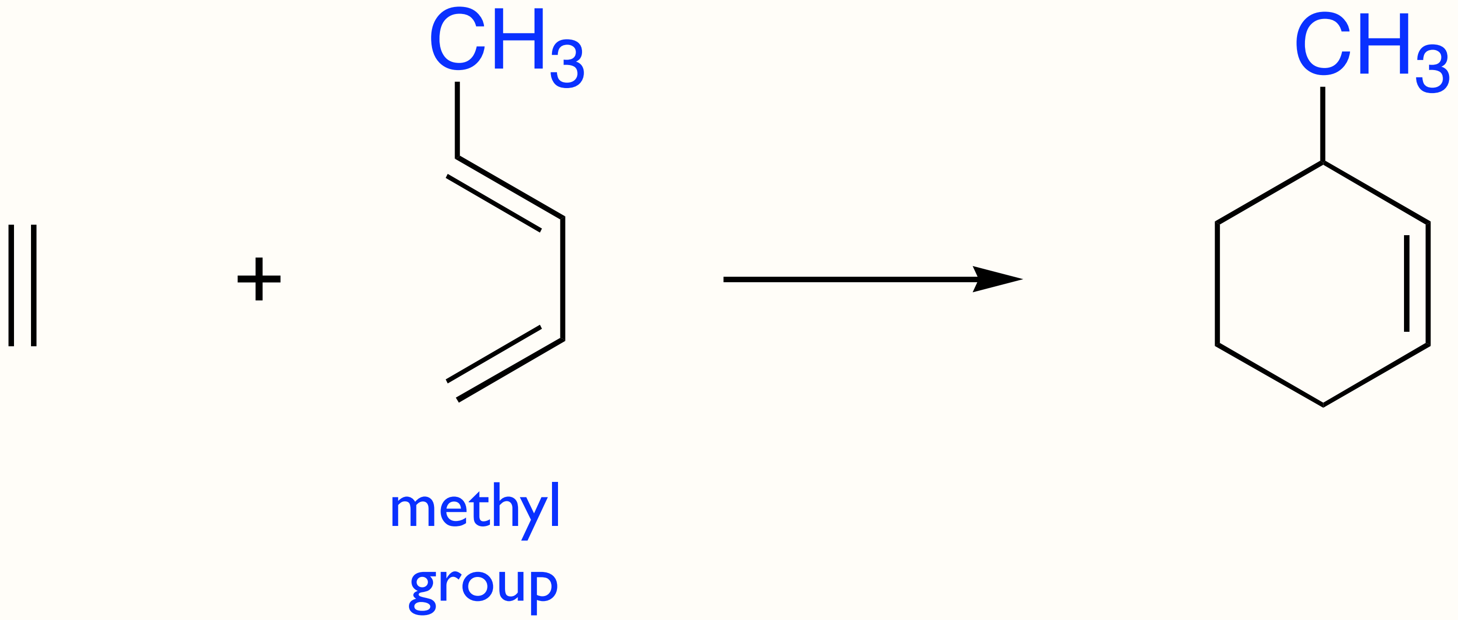
Electron withdrawing groups (EWG) increase the reactivity of the dienophile = faster reaction

Reactivity of Diels Alder



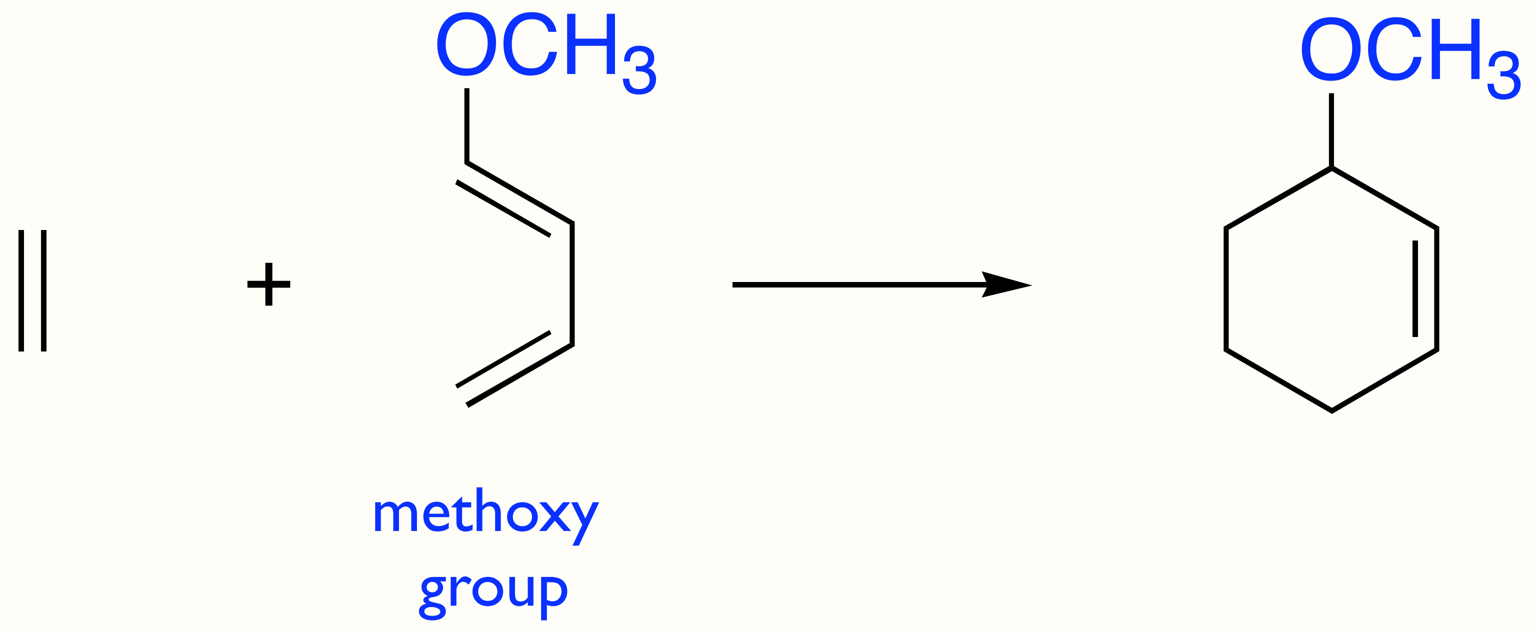
Electron donating groups (EDG) increase the reactivity of the diene = faster reaction

Reactivity of Diels Alder



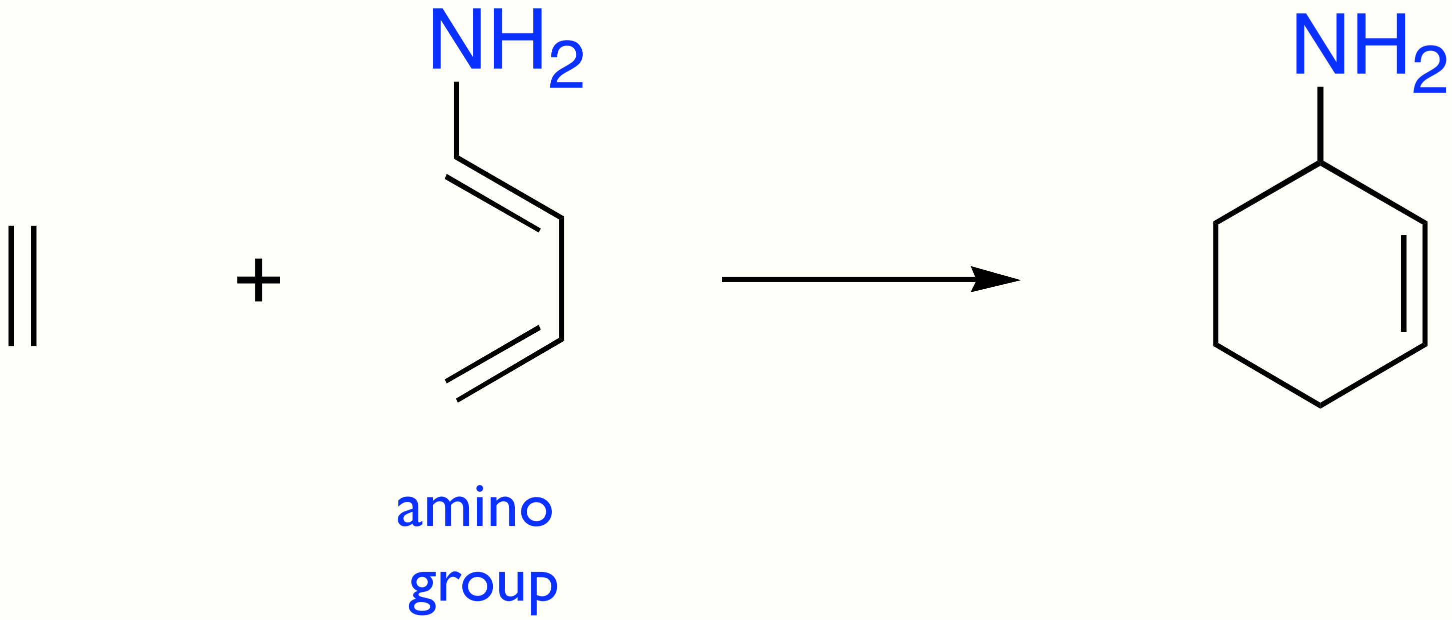
Electron donating groups (EDG) increase the reactivity of the diene = faster reaction

Reactivity of Diels Alder



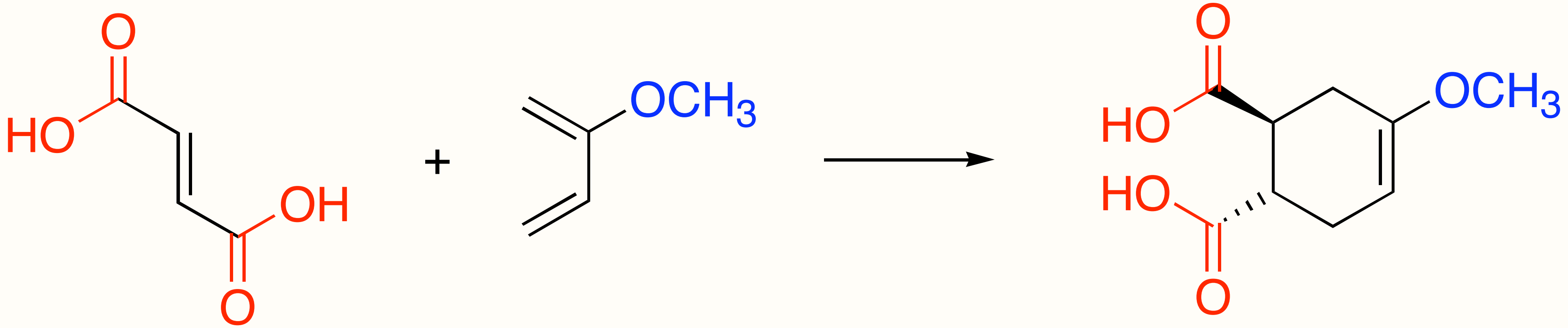
Electron donating groups (EDG) increase the reactivity of the diene = faster reaction

Reactivity of Diels Alder



Electron donating groups (EDG) increase the reactivity of the diene = faster reaction

Reactivity of Diels Alder

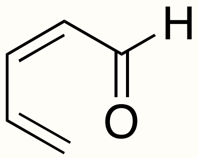


Fastest reaction have both an EWG on the dienophile and an EDG on the diene. We'll discover why next week.

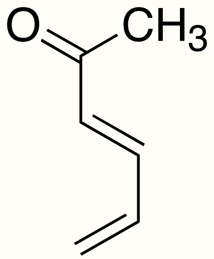
Self Test Question

Which of the following dienes or dienophiles would be the *least reactive* in a Diels-Alder reaction?

[✓ A]



[✓ B]



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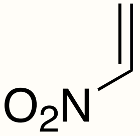
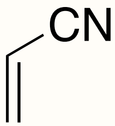
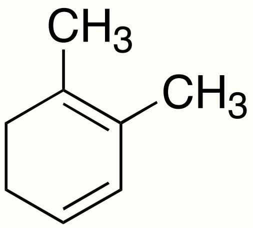
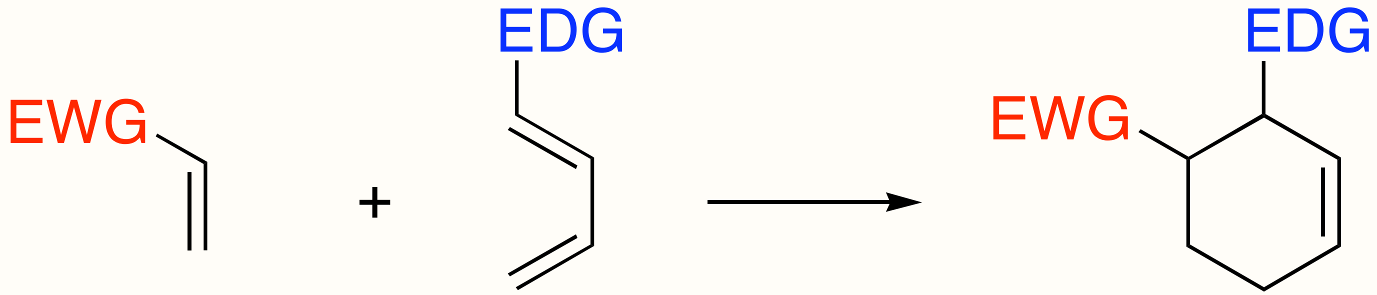


D



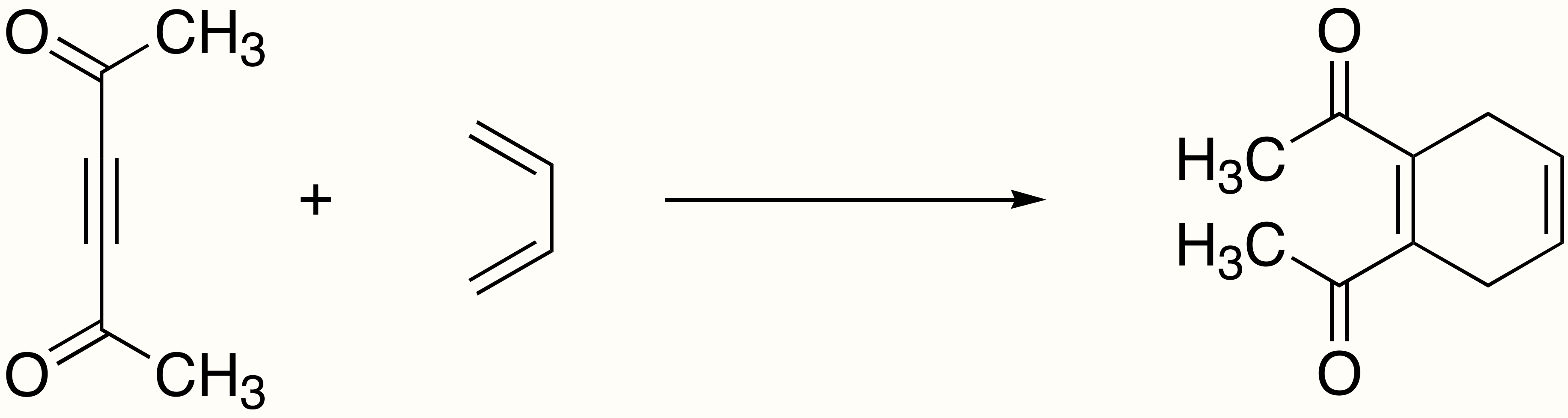
E





Diels Alder Reaction

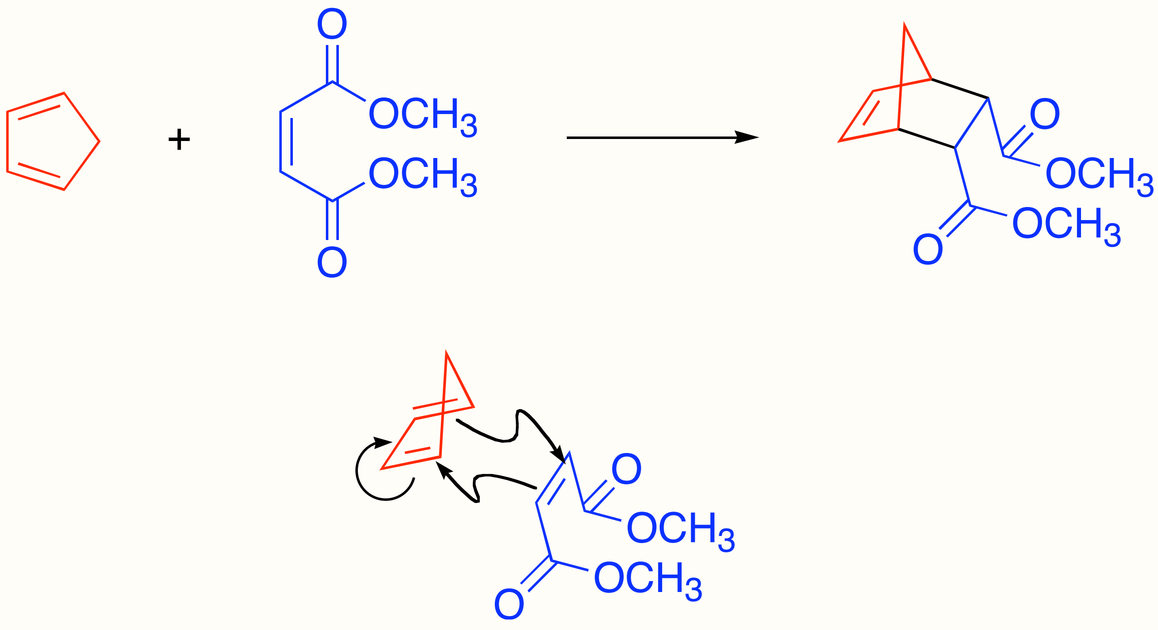
More complex examples…



Alkynes can also participate as a dienophile as long as the y are activated with EWGs

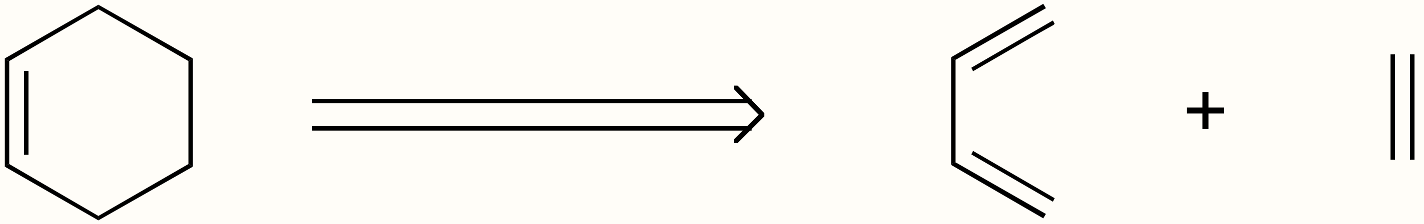
Diels Alder Reaction

More complex examples…



Cyclic dienes gives bridged bicylco Diels Alder adducts

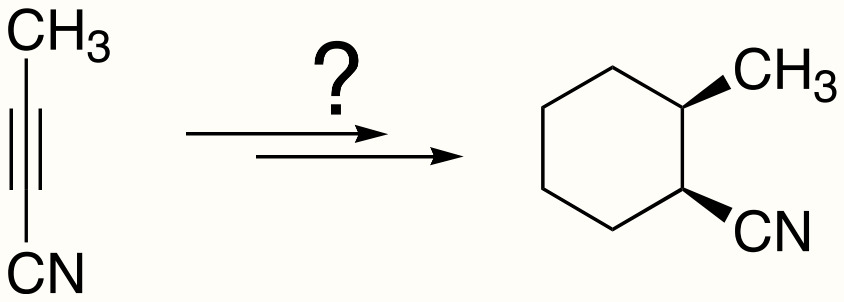
Diels Alder in Synthesis

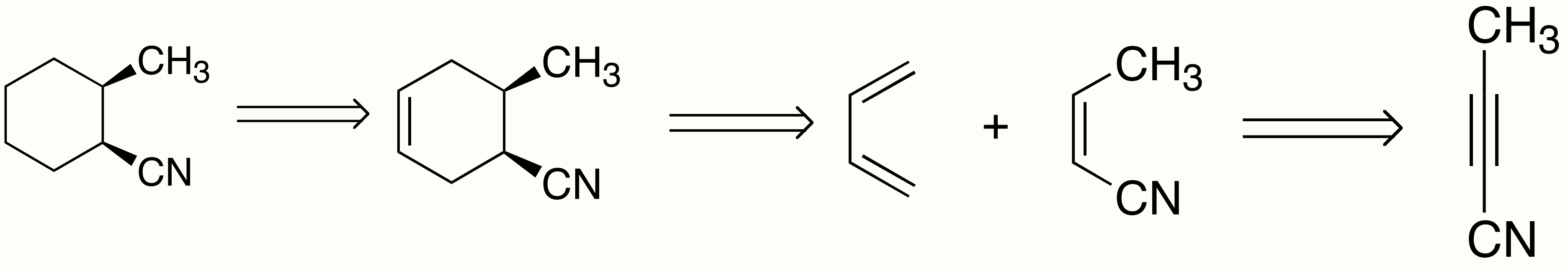


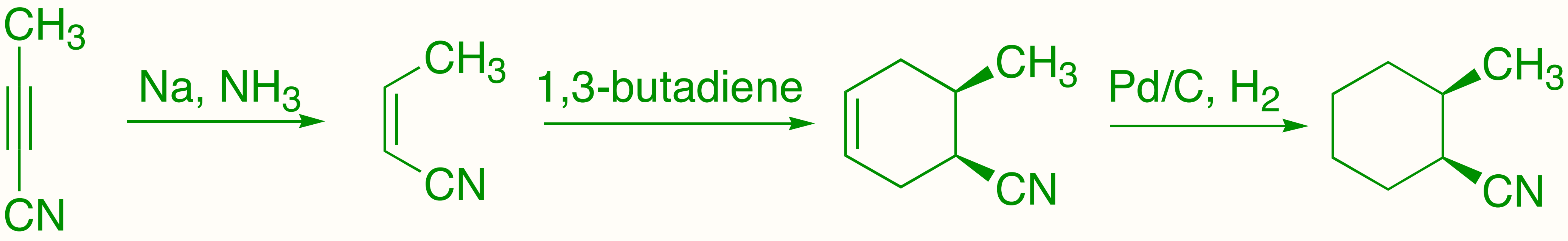
diene dienophile

Molecules with cyclohexene rings can often be made through Diels-Alder reaction

Synthesis Example

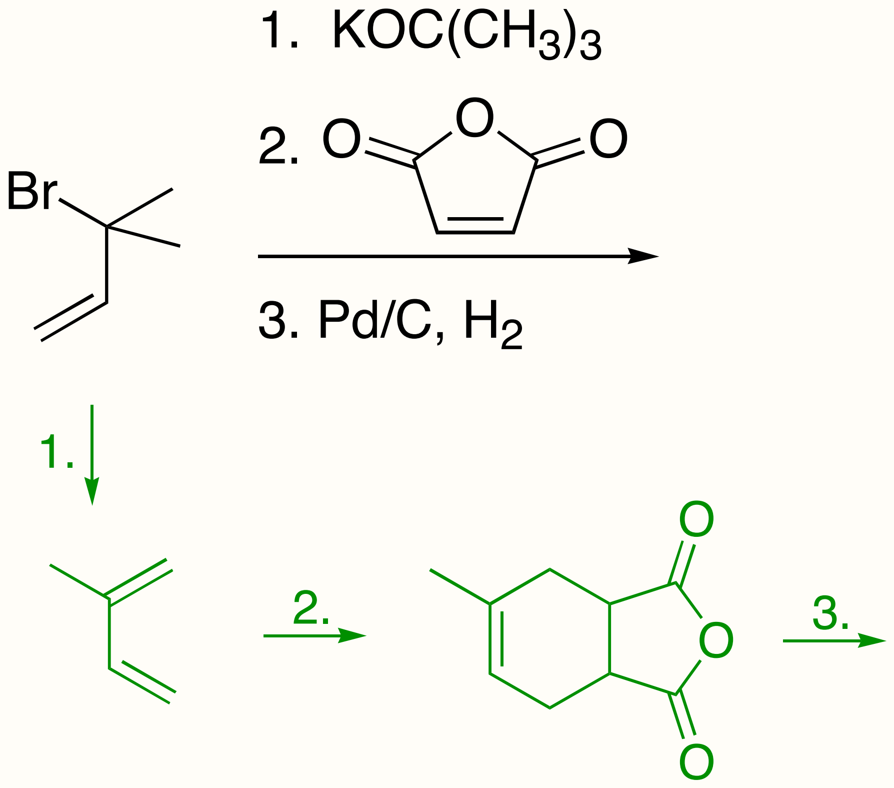






Self Test Question

Predict the product.

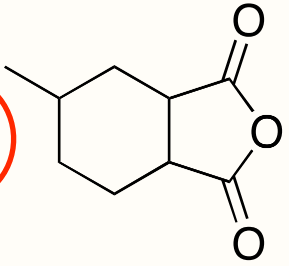


1. KOC$(CH_3)_3$

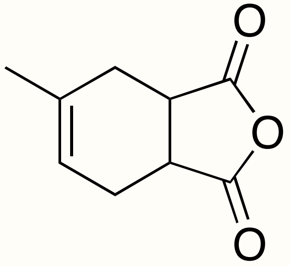
2.

3. Pd/C, H_2

[✓ A]



B



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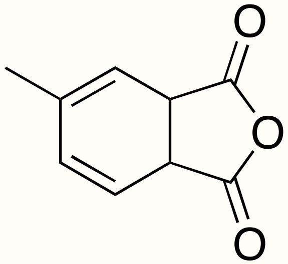

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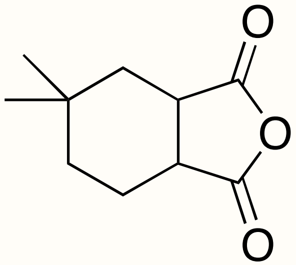

Next Lecture...

Chapter 10: Sections 10.16 & 10.17
Chapter 11: Sections 11.1-11.9

Quiz Next Week. . .

Chapter 10 & Synthesis Problems

Exam Two

- Monday, April 5
- 6:00-7:15 p.m.
- 250 SES
- Chapters 6-10 (everything!)
- Makeup Exam: Monday, April 12th, time t.b.a.

<u>Makeup policy:</u> There are no makeup exams without **prior** approval. Only students showing proof of a class conflict will have the option to take a makeup exam. To be added to the makeup list, you must email me no later than Friday, Feb. 12.

Exam One Grade Distribution

Q1. Ranking (50 points)

Q2. Predict the Products (50 points)

Q3. Arrow-Pushing Mechanism (50 points)

Q4. Nomenclature (20 points)

Q5. Drawing & Conformational Analysis (50 points)

Q6. Functional Groups (30 points)

Exam One Policies

- Non-scientific calculators allowed only
- No cell phones, ipods or others electronic devices
- No molecular models
- Periodic table will be provided
- Seating will be assigned
- **Bring Your I.D.**