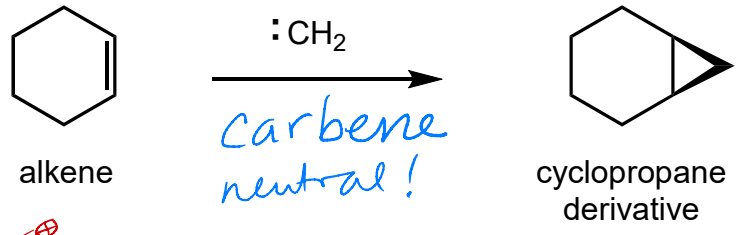
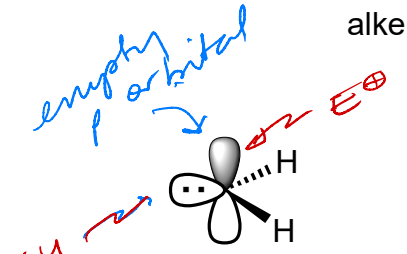
Chapter 6 Cyclic Target Molecules

6.1 Synthesis of Cyclopropane Rings

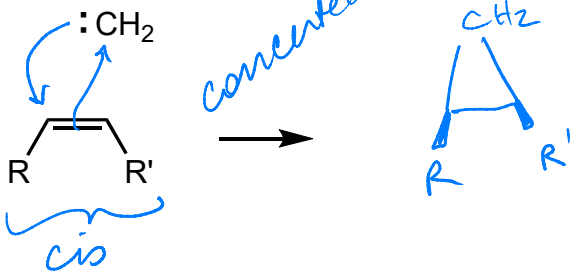




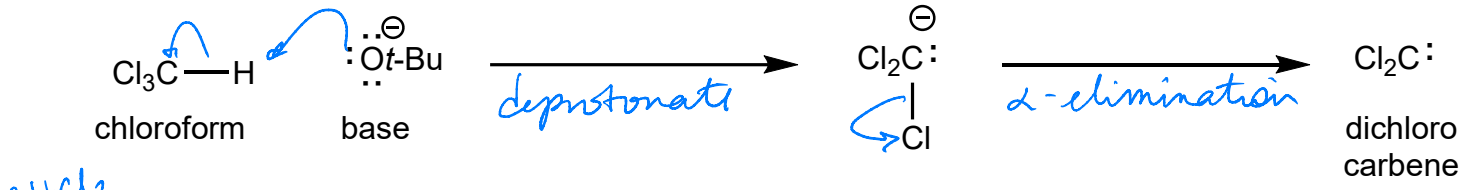
"singlet" carbene

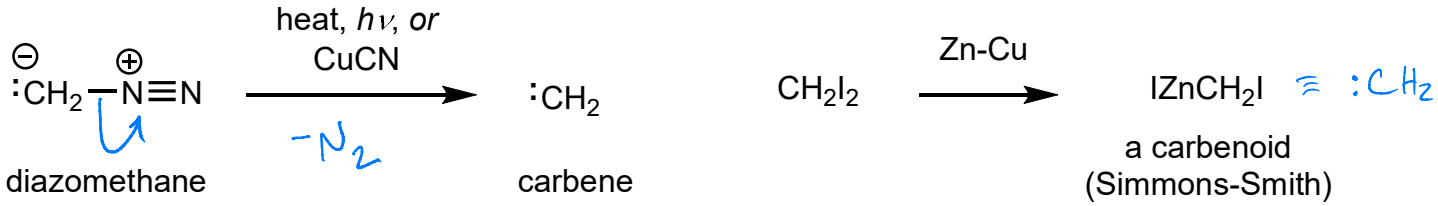
has paired electrons

~sp² hybridized carbon

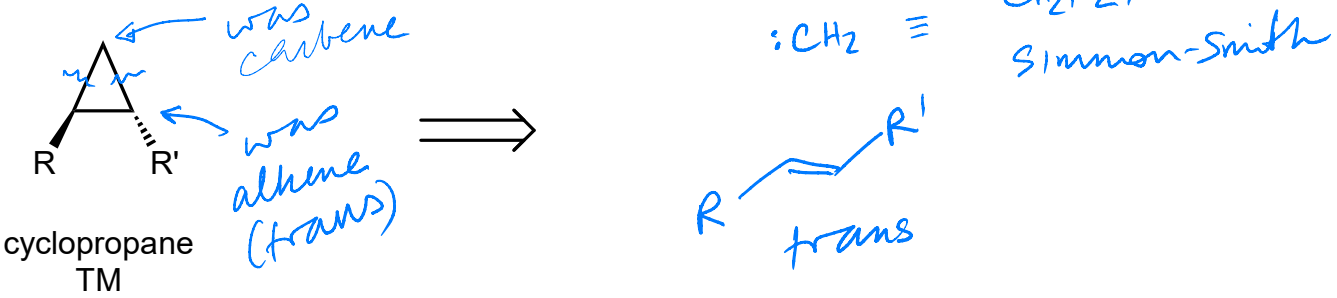


Methods for preparing singlet carbenes

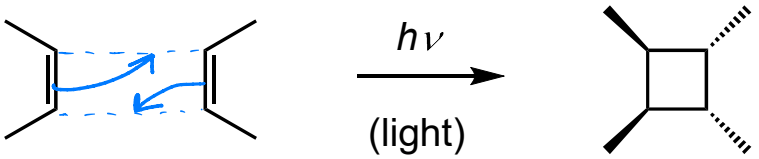




Retrosynthesis of a cyclopropane TM



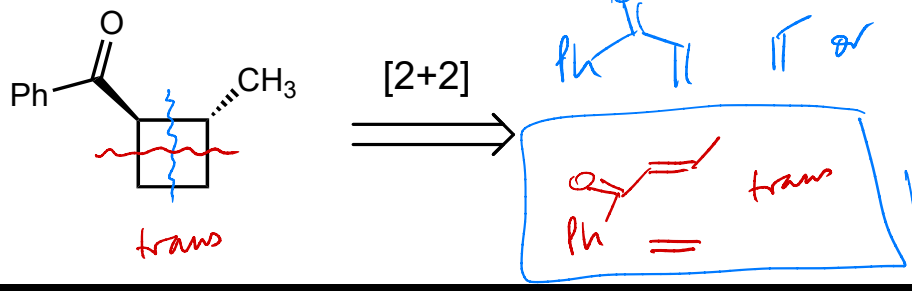
6.2 Synthesis of Cyclobutane Rings



[2+2] cycloaddition

pericyclic reaction

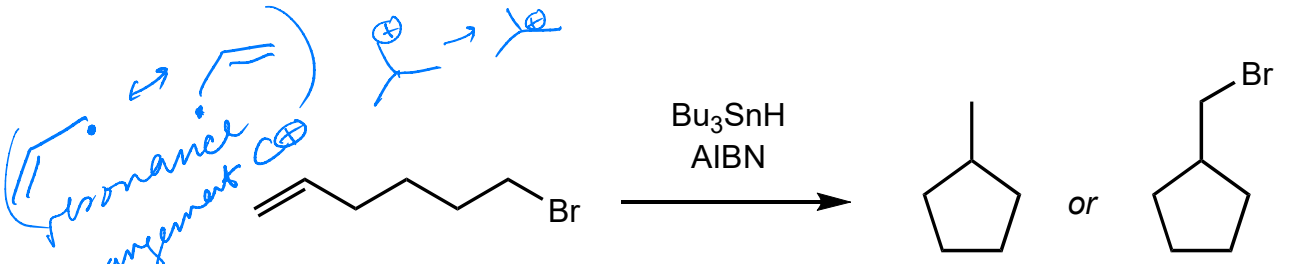
Retrosynthesis of cyclobutane ringes



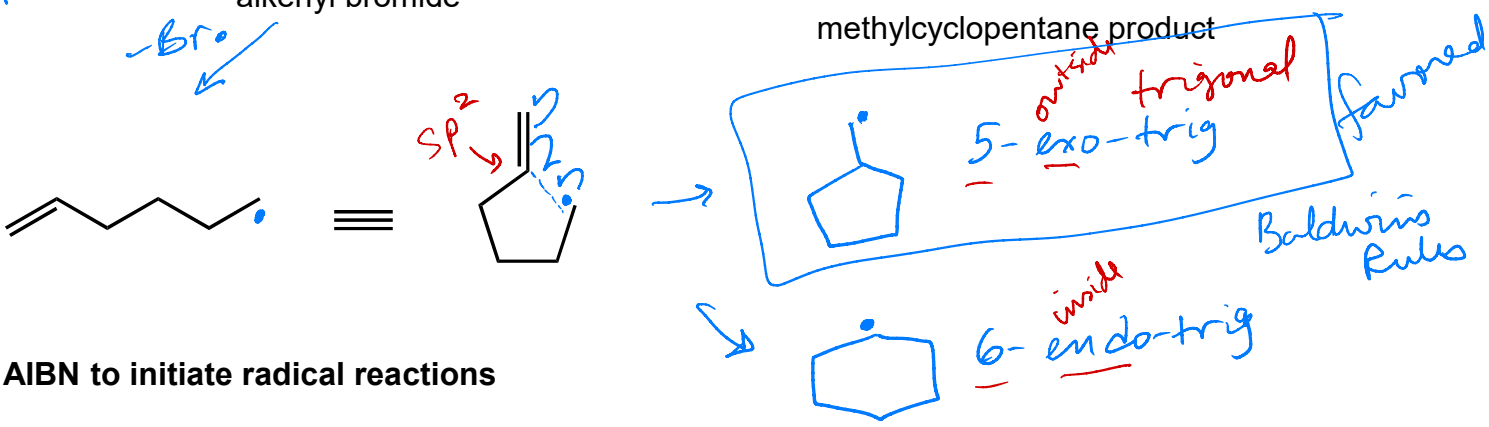
+ stereo isomers

6.3 Synthesis of Cyclopentane Rings via Radical Cyclization

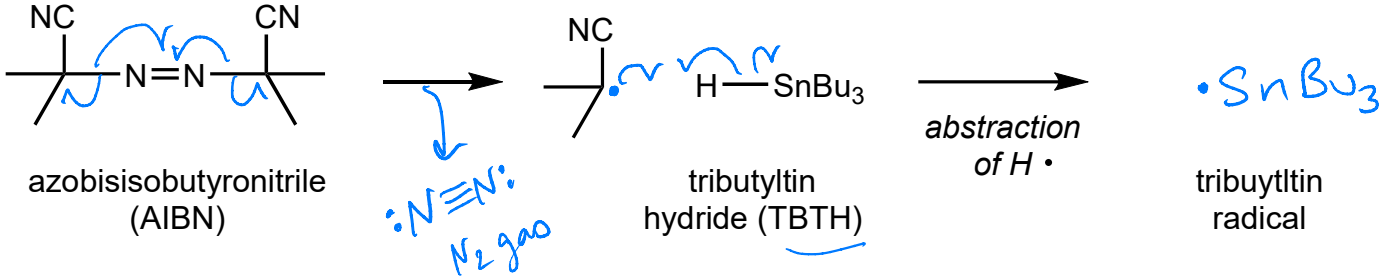
cyclization reactions to form 5- or 6-membered rings are favorable because of low ring strain

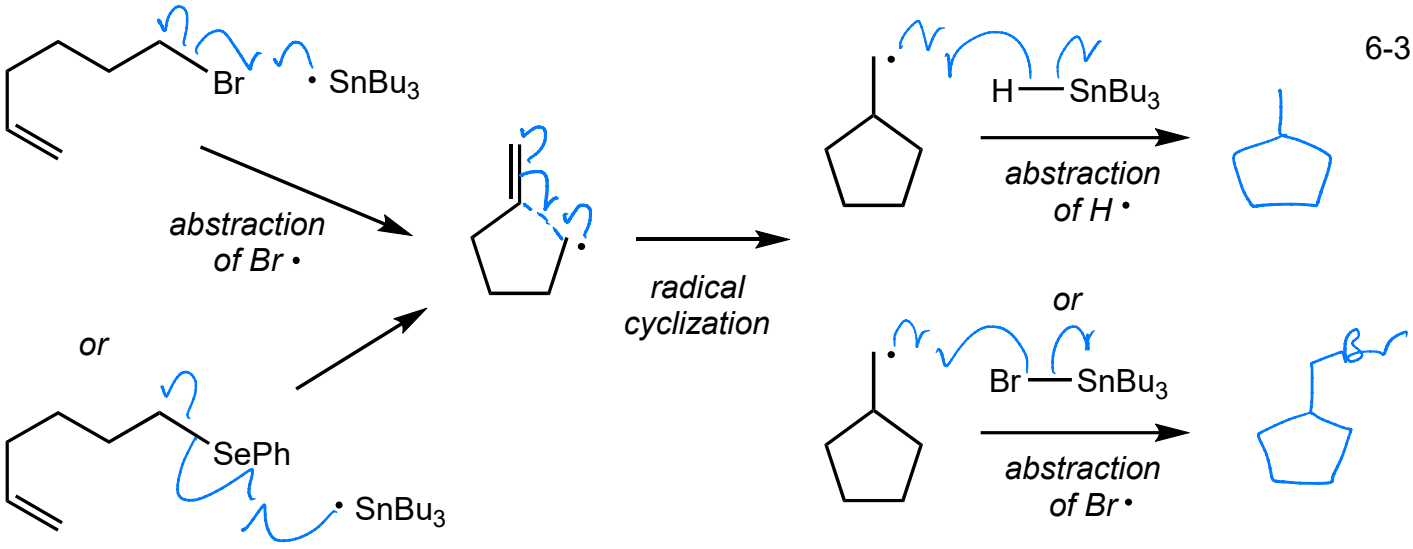


resonance rearrangement



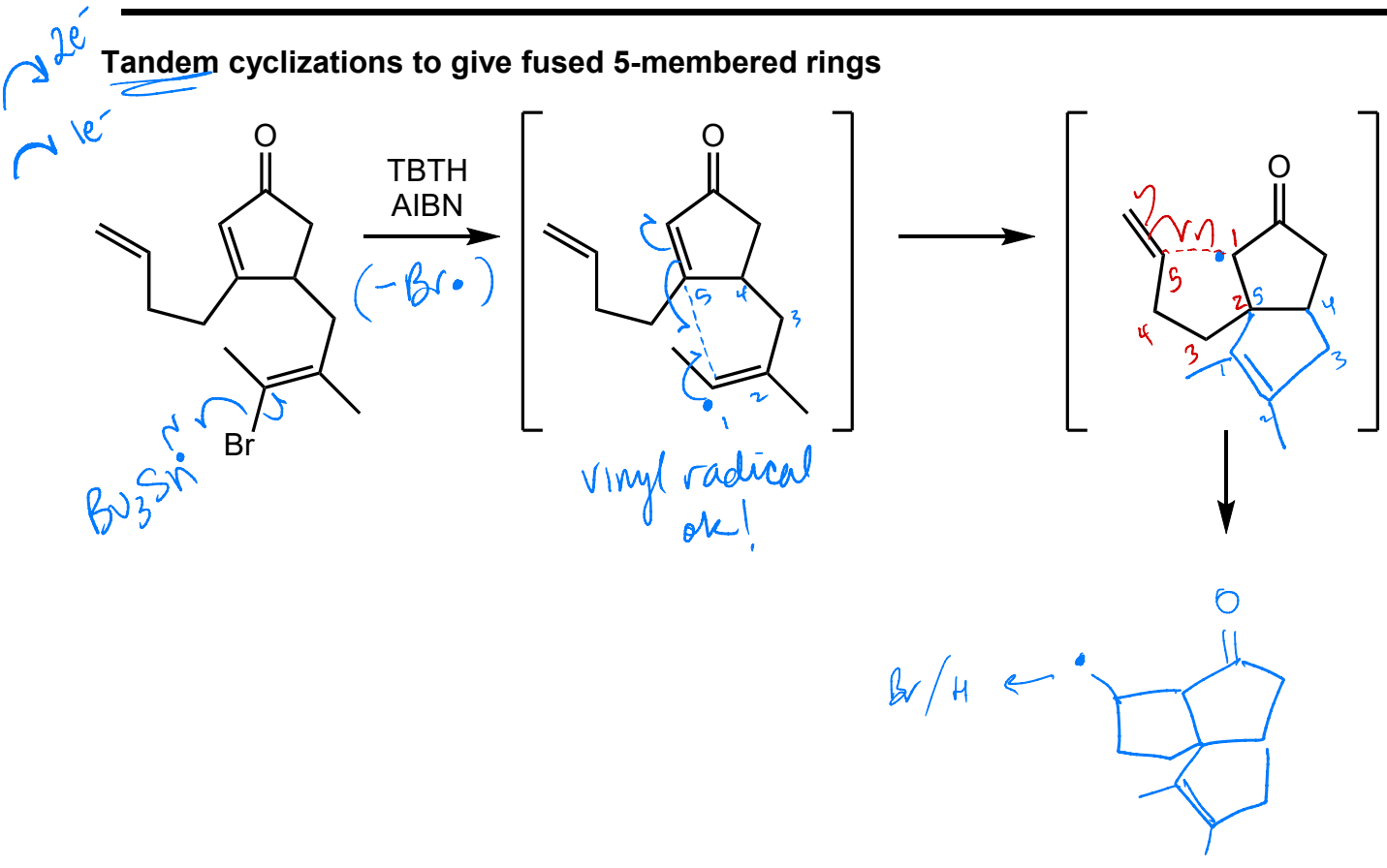
AIBN to initiate radical reactions





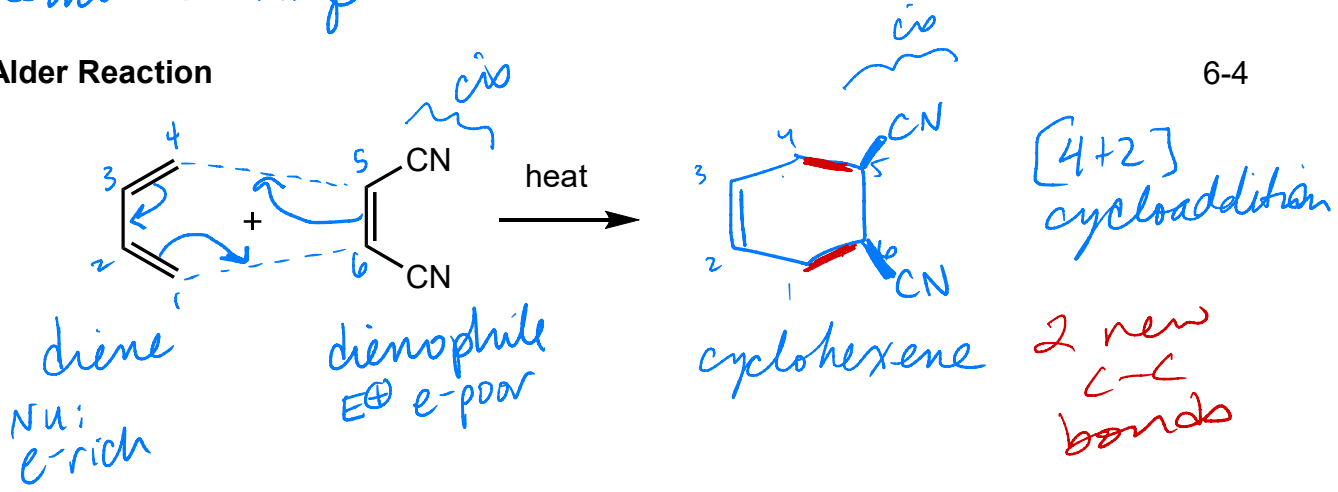
Retrosynthesis of methylcyclopentane rings

Tandem cyclizations to give fused 5-membered rings

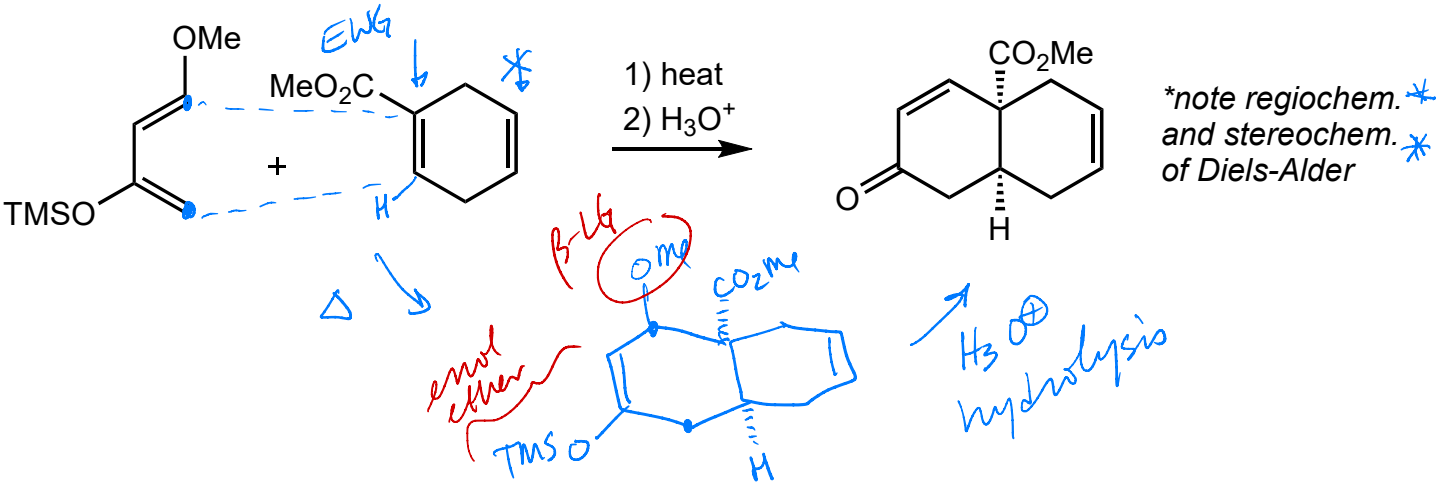


6.4 6-membered rings

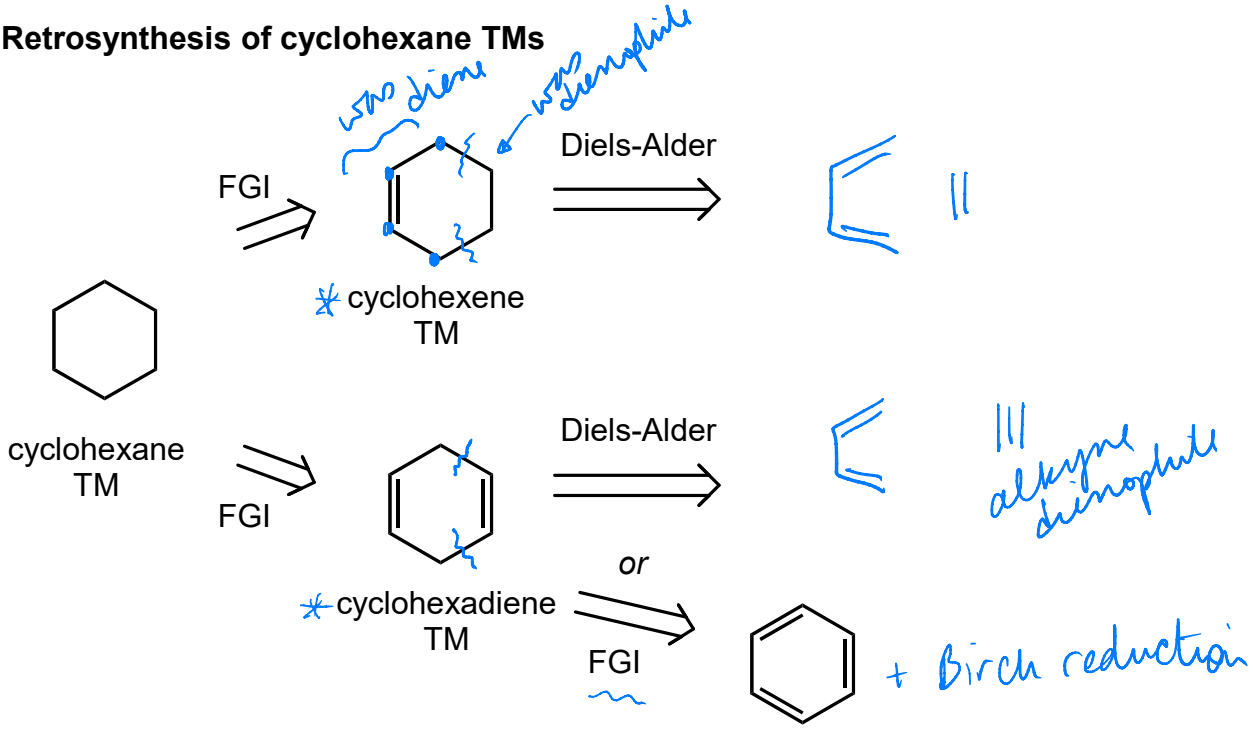
The Diels-Alder Reaction



Danishefsky's Diene is a useful synthetic reagent (see problems 6-3 and 6-8)

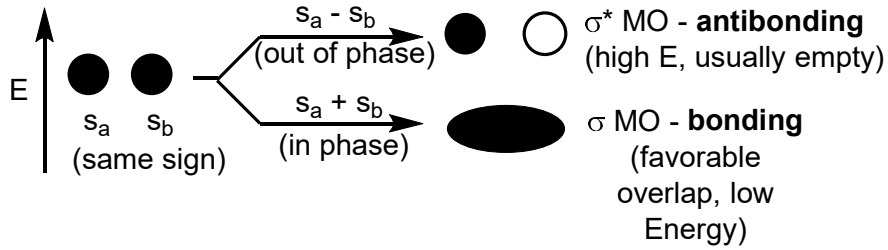


Retrosynthesis of cyclohexane TMs

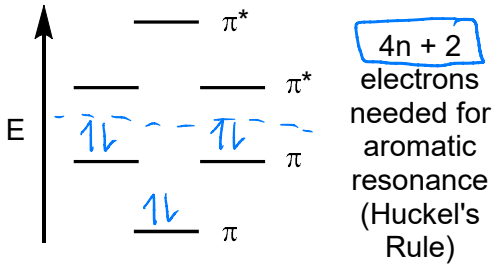


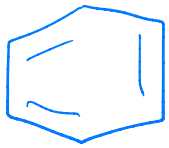
Molecular Orbital (MO) Theory to Explain Pericyclic Reactions

Molecular Orbital theory of bonding

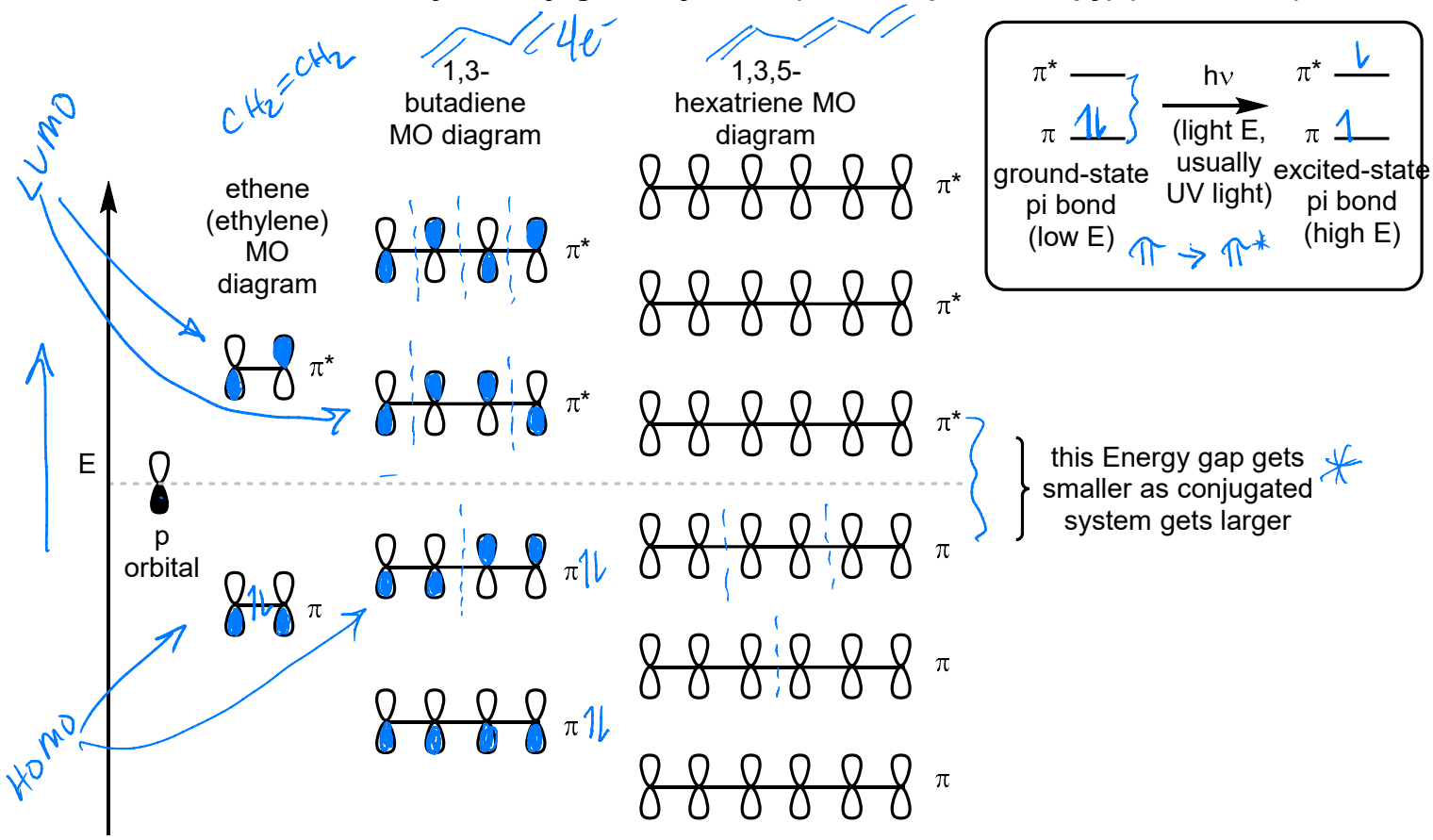


MO theory of aromaticity





Molecular Orbital theory of conjugated systems (UV-Vis Spectroscopy) (Klein 16.11)

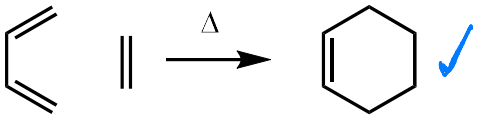


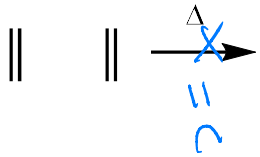
if...**increase** in # of conjugated pi bonds
then...**increase** in resonance stabilization
and...**decrease** in E needed for π → π*

lower Energy **visible light** is absorbed so these compounds are **COLORED!**

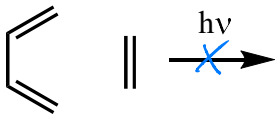
MO theory of pericyclic reactions (the Woodward-Hoffmann rules) (Klein 16.8)

Heat-promoted pericyclic reactions

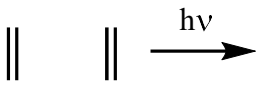




Light-promoted pericyclic reactions



4+2 cycloadditions are thermally ~~/photochemically~~ allowed

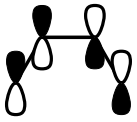


2+2 cycloadditions are ~~thermally/~~photochemically allowed

HOMO = Highest occupied M.O.
LUMO = Lowest Unoccupied m.O.

n.u.: e⁻ donor

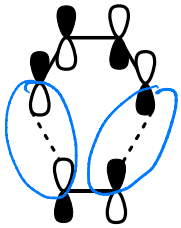
Butadiene
HOMO (π)



+

Ethene
LUMO (π*)

E^+ e⁻ acceptor



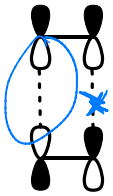
orbital symmetry is conserved

thermal [4+2] cycloaddition is allowed ✓

Ethene
HOMO (π)

+

Ethene
LUMO (π*)

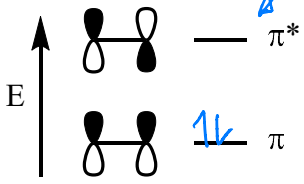


orbital symmetry is NOT conserved

thermal [2+2] cycloaddition is forbidden

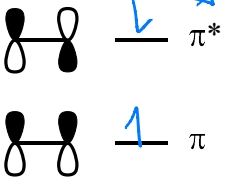
Ethene MO's
(ground state)

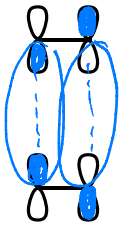
LUMO



Ethene MO's
(excited state)

HOMO!



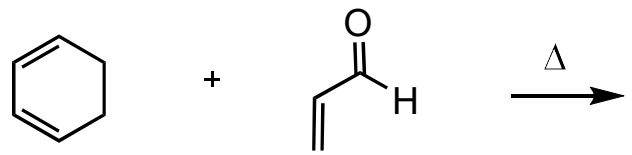


HOMO of excited state

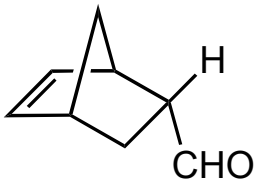
LUMO of groundstate

photochemical [2+2] cycloaddition is symmetry-allowed ✓

Predict the major product expected.

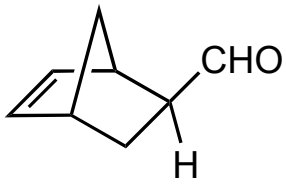


A)



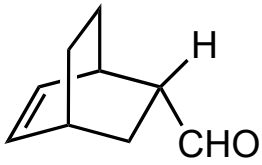
+ enantiomer

B)



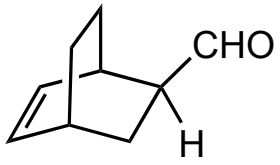
+ enantiomer

C)



+ enantiomer

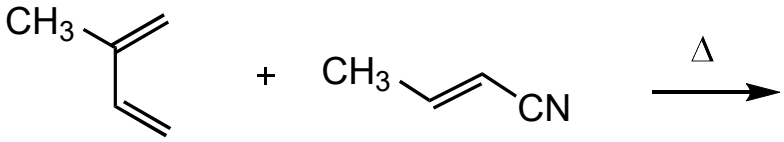
D)



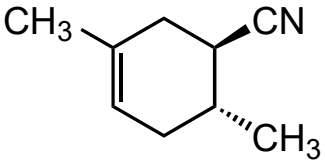
+ enantiomer

E) none of the above

Predict the major product expected.

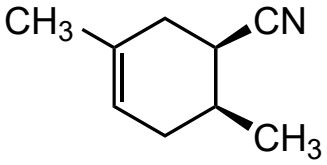


A)



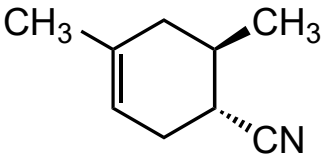
+ enantiomer

B)



+ enantiomer

C)



D)