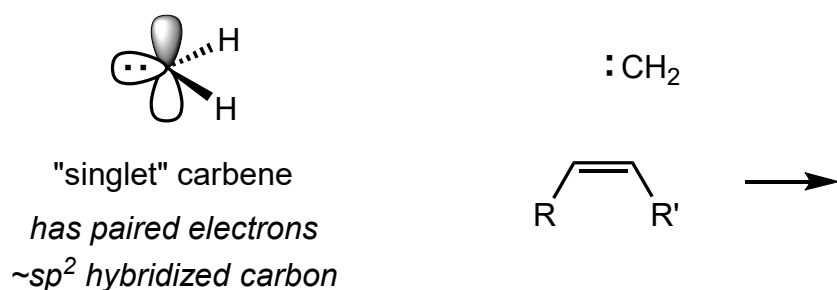
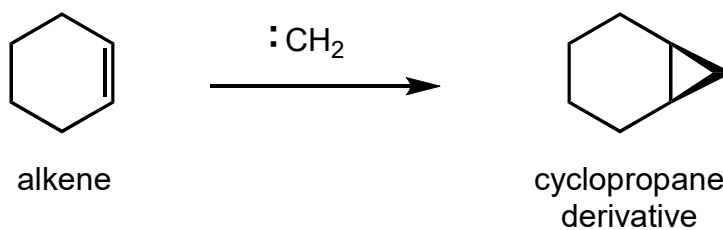
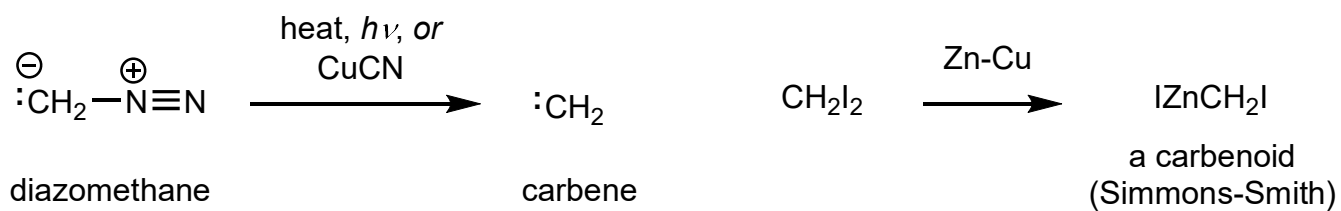
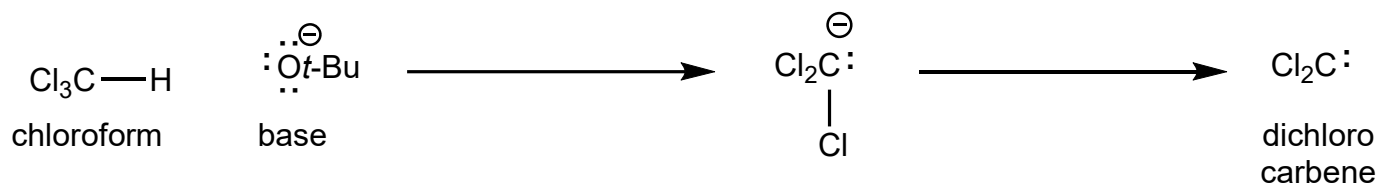


Chapter 6 Cyclic Target Molecules

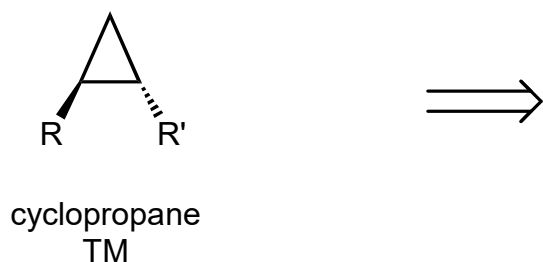
6.1 Synthesis of Cyclopropane Rings



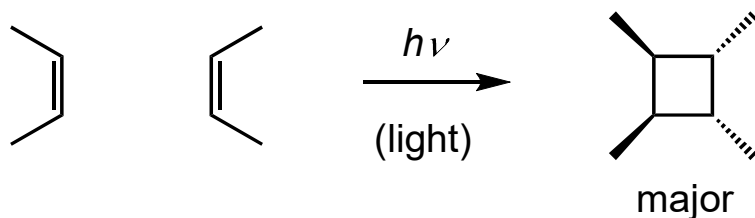
Methods for preparing singlet carbenes



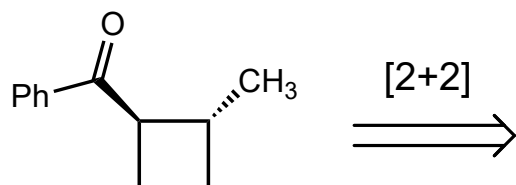
Retrosynthesis of a cyclopropane TM



6.2 Synthesis of Cyclobutane Rings

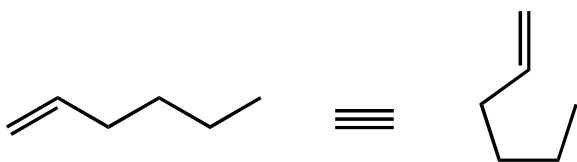
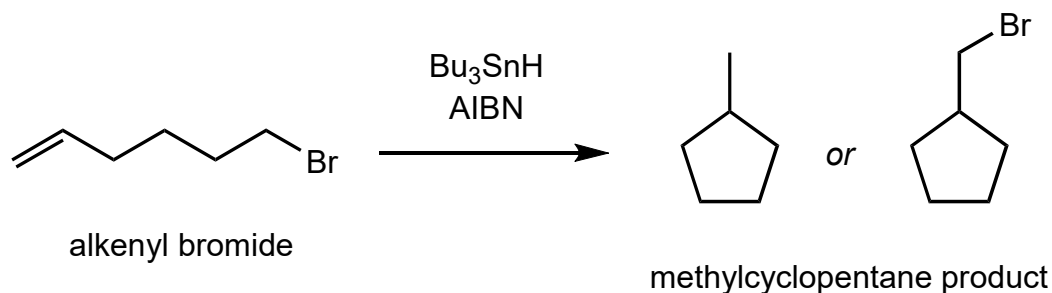


Retrosynthesis of cyclobutane rings

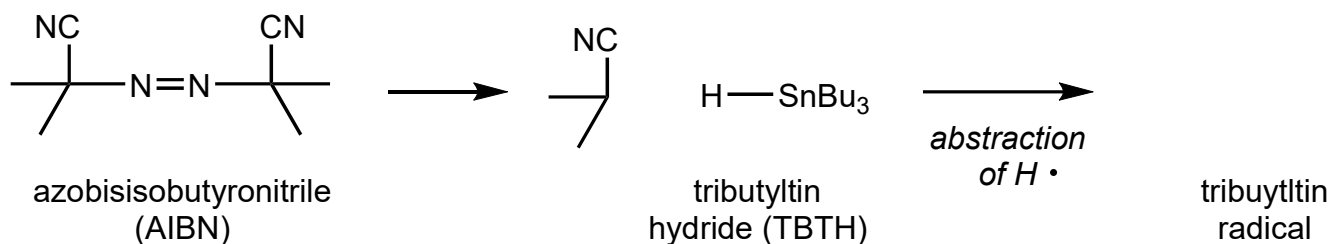


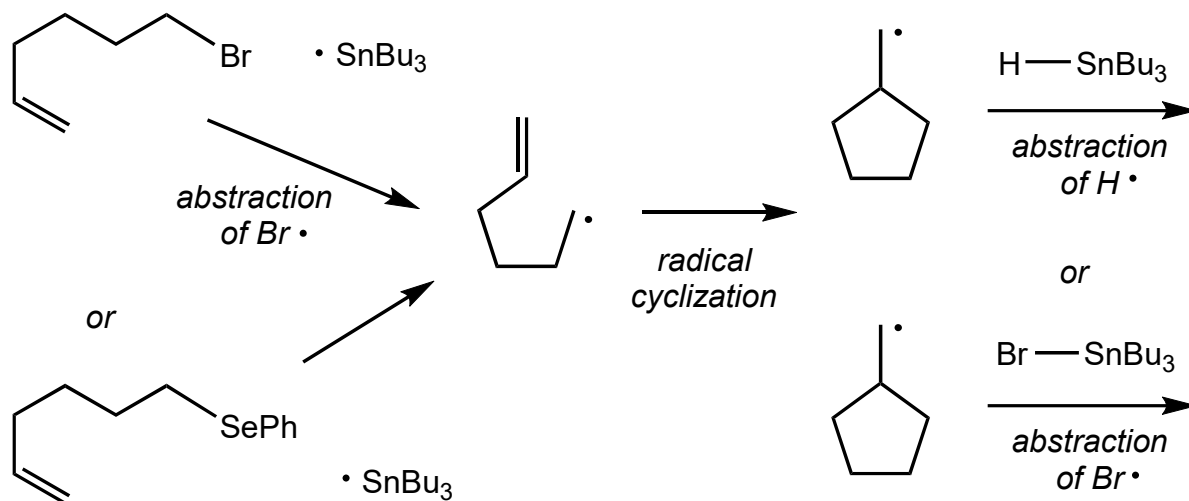
6.3 Synthesis of Cyclopentane Rings via Radical Cyclization

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

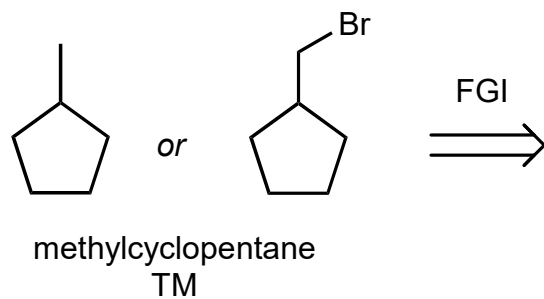


AIBN to initiate radical reactions

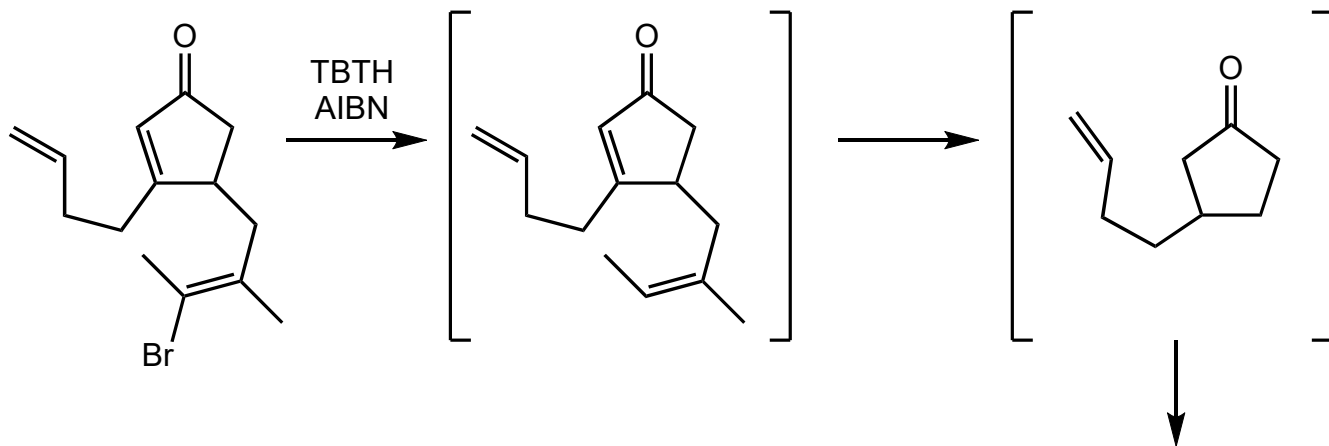




Retrosynthesis of methylcyclopentane rings



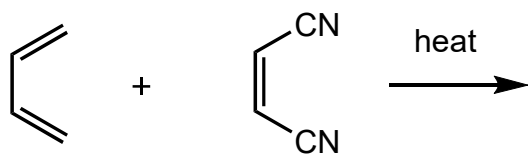
Tandem cyclizations to give fused 5-membered rings



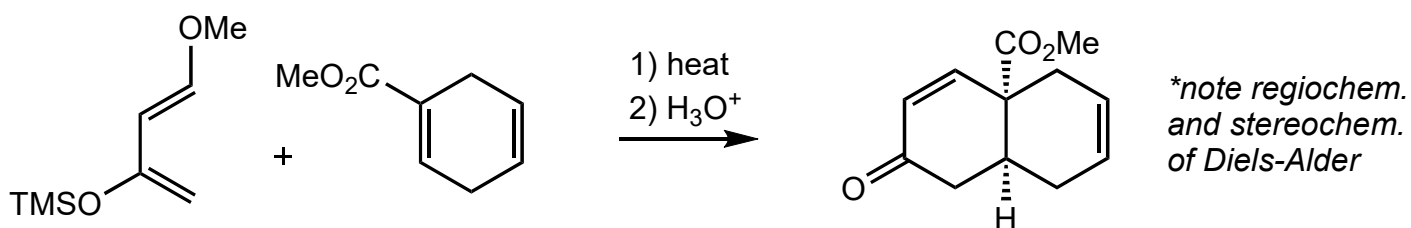
6.4 Synthesis of 6-Membered Rings

6-4

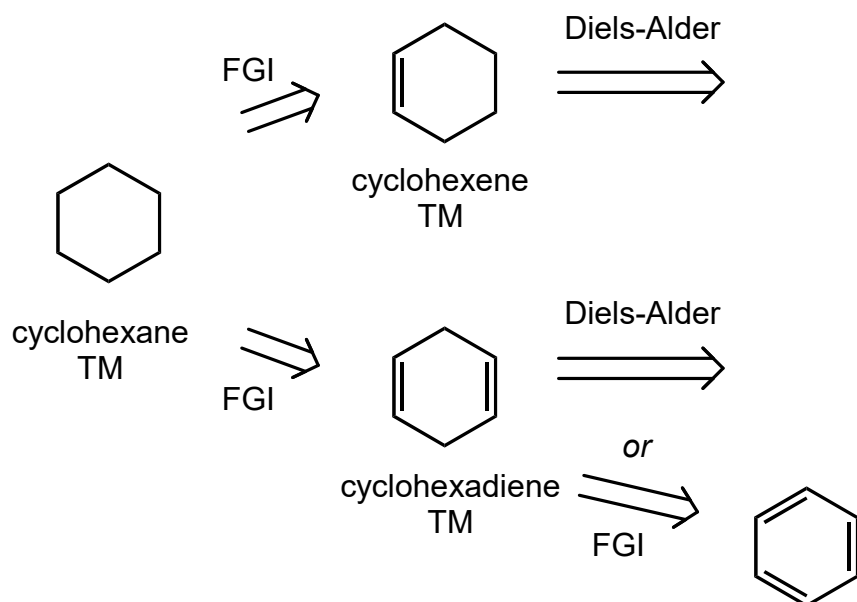
The Diels-Alder Reaction



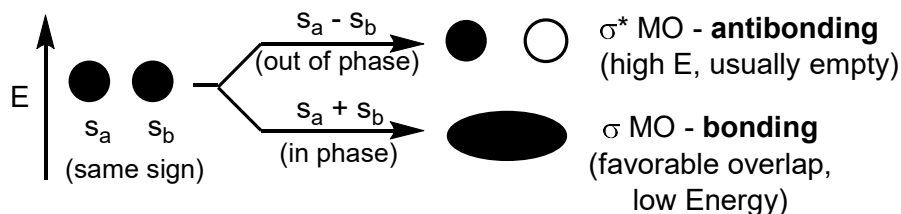
Danishesky's Diene is a useful synthetic reagent (see problems 6-3 and 6-8)



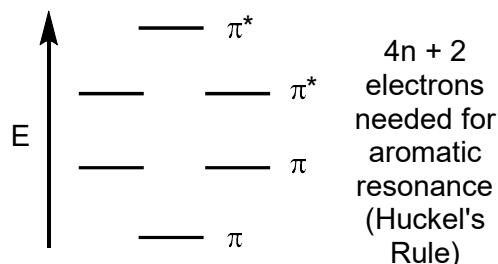
Retrosynthesis of cyclohexane TMs



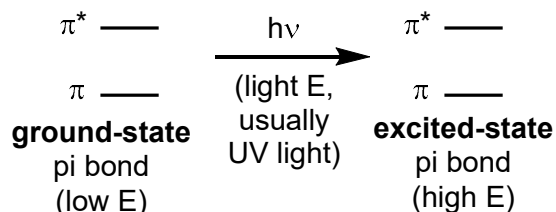
Molecular Orbital theory of bonding



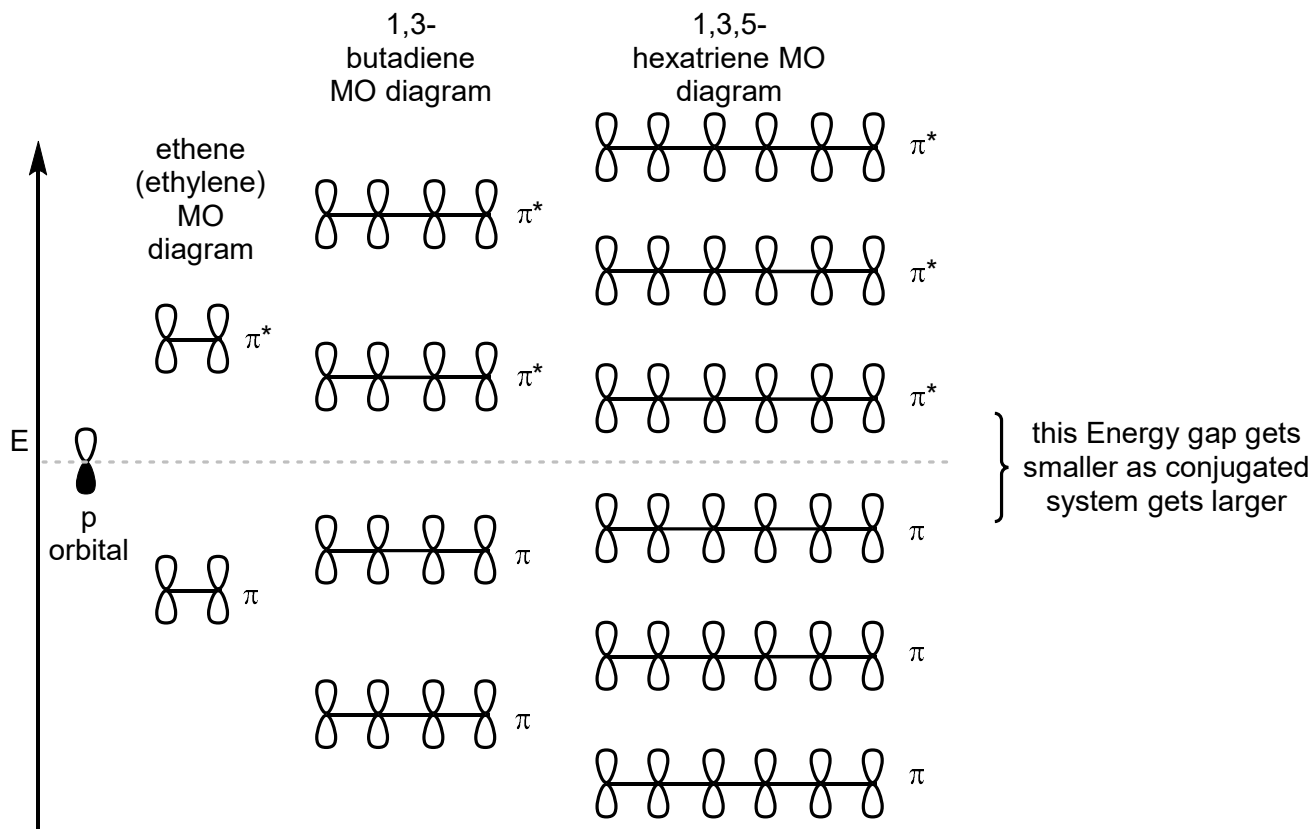
MO theory of aromaticity



MO theory of Ultraviolet/Visible Spectroscopy



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

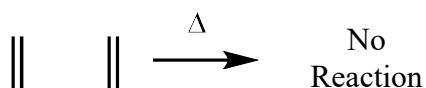
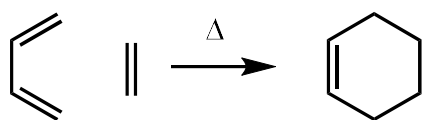


if...**increase** in # of conjugated pi bonds
 then...**increase** in resonance stabilization
 and...**decrease** in E needed for $\pi \rightarrow \pi^*$

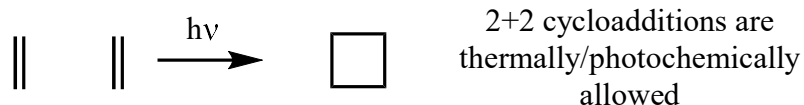
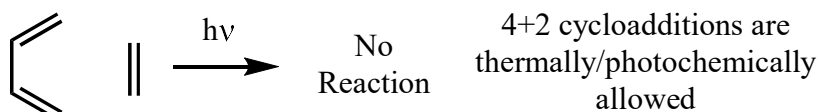
lower Energy **visible light** is absorbed so these compounds are **COLORED!**

MO theory of pericyclic reactions (the Woodward-Hoffmann rules) (Klein 16.8)⁶⁻⁶

Heat-promoted pericyclic reactions



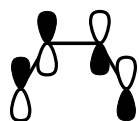
Light-promoted pericyclic reactions



4+2 cycloadditions are thermally/photochemically allowed

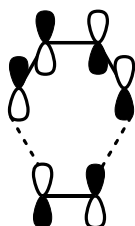
2+2 cycloadditions are thermally/photochemically allowed

Butadiene
HOMO (π)



+

Ethene
LUMO (π^*)



*orbital
symmetry is
conserved*



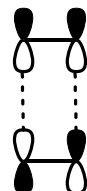
thermal [4+2]
cycloaddition
is allowed

Ethene
HOMO (π)



+

Ethene
LUMO (π^*)

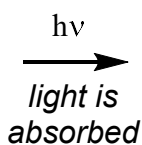
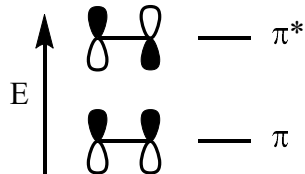


*orbital symmetry is
NOT conserved*

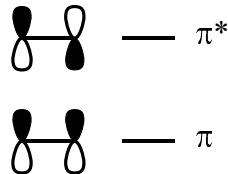


thermal [2+2]
cycloaddition
is forbidden

Ethene MO's
(ground state)



Ethene MO's
(excited state)



HOMO of
excited state

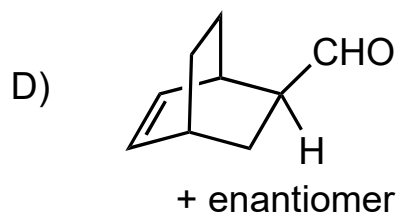
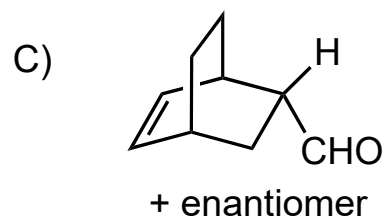
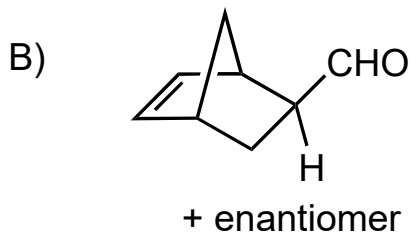
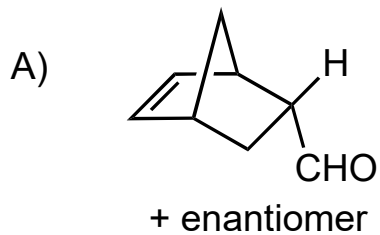
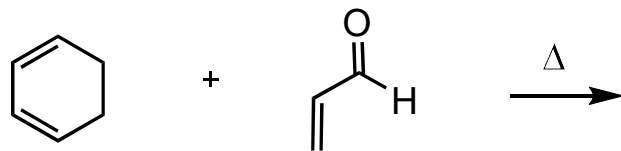


LUMO of
groundstate



photochemical [2+2]
cycloaddition is
symmetry-allowed

Predict the major product expected.



E) none of the above

Predict the major product expected.

