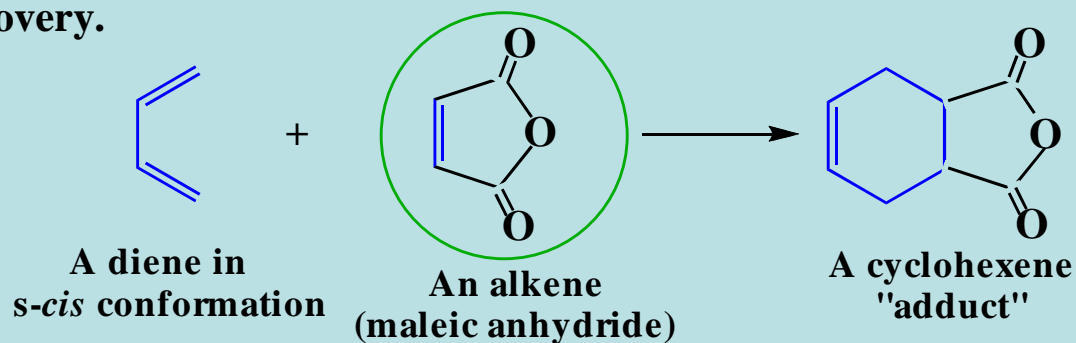


The Diels-Alder Reaction

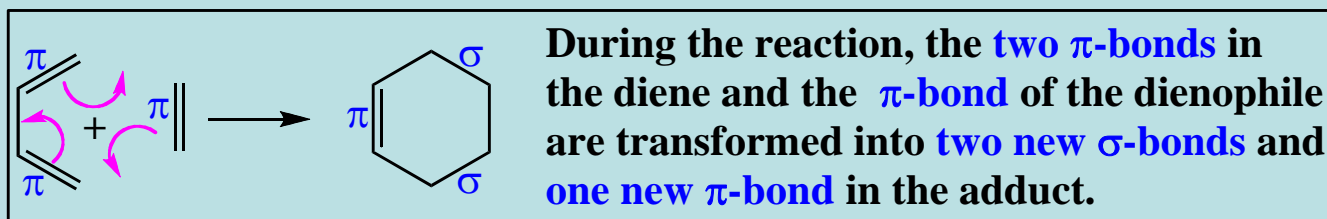
A 1,4-Cycloaddition Reaction of Dienes

A very useful **cycloaddition addition** reaction of 1,3-dienes and alkenes to produce **cyclohexenes** was discovered in 1928 by Otto Diels and Kurt Alder. They received the Nobel Prize in Chemistry in 1950 for this discovery.



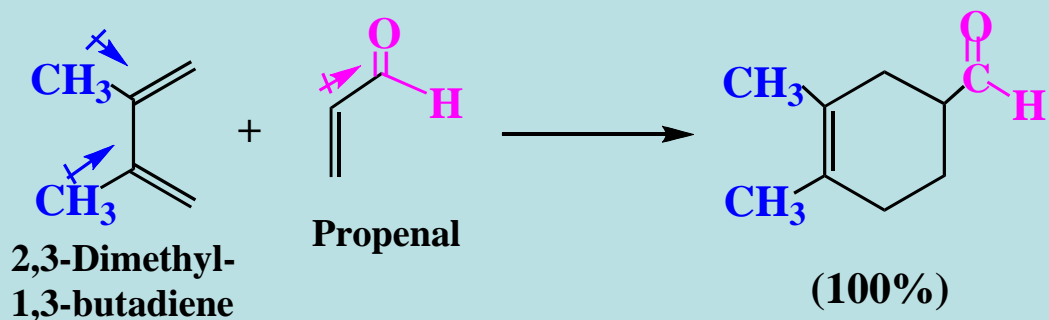
This is an example of a **4 + 2 π -electron cycloaddition**.

It involves a conjugated diene (a 4 π -electron system) and an alkene (a 2 π -electron system). The latter is called a **dienophile**.

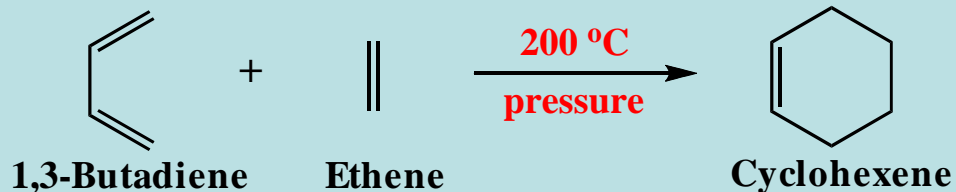


Factors Favoring the Diels-Alder Reaction

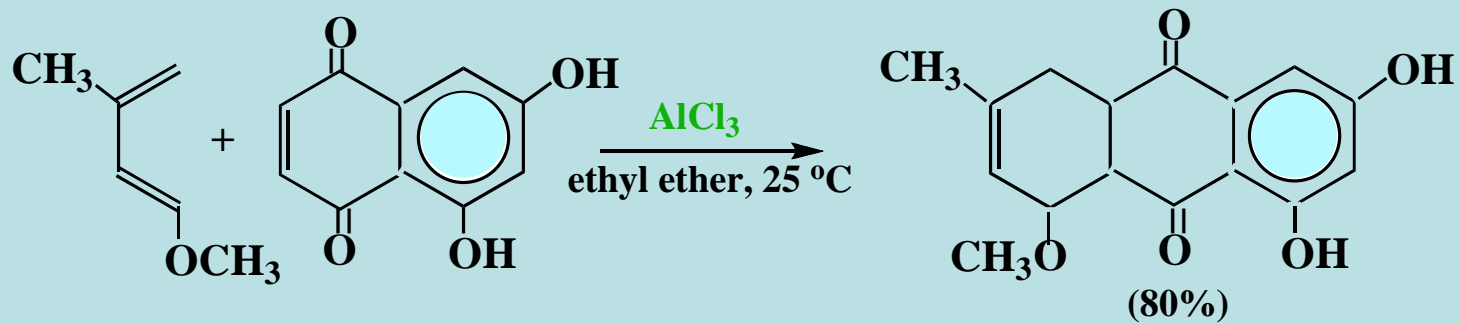
This cycloaddition reaction is promoted by **electron-withdrawing groups in the dienophile** and **electron-releasing groups in the diene**.



The Diels-Alder reaction is enhanced by **high temperature and pressure**.

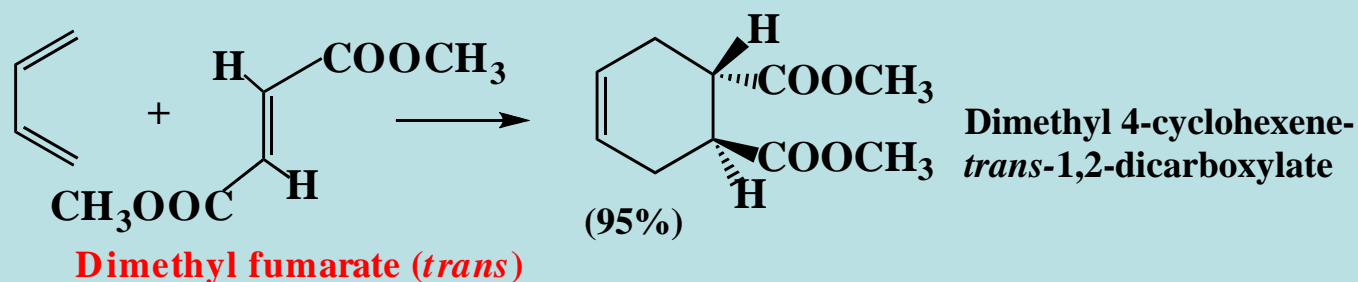
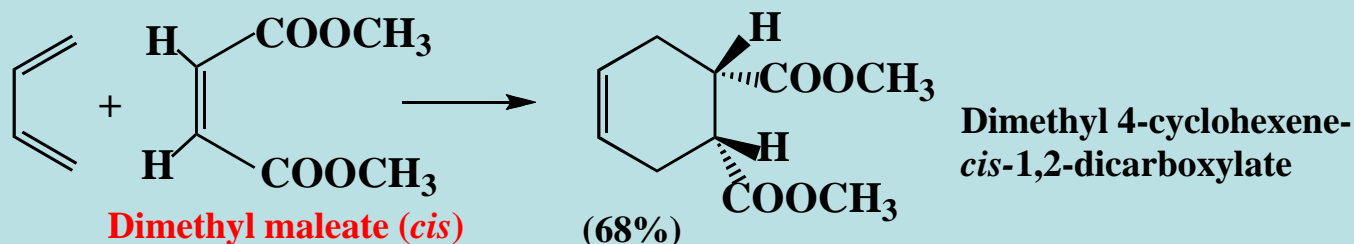


The Diels-Alder reaction is enhanced by the presence of **Lewis acids**.



Stereochemistry of the Diels-Alder Reaction

- (1) The Diels-Alder reaction is a **syn addition** and **the configuration of the dienophile is retained** in the product.



NOTE: The pair of dienophiles above are among the very few geometric isomers that have different names (maleate vs. fumarate) and do not require use of *cis/trans* or *Z/E* designations.

- (3) Cyclic dienes, such as cyclopentadiene, give *endo* products in the Diels-Alder reaction.

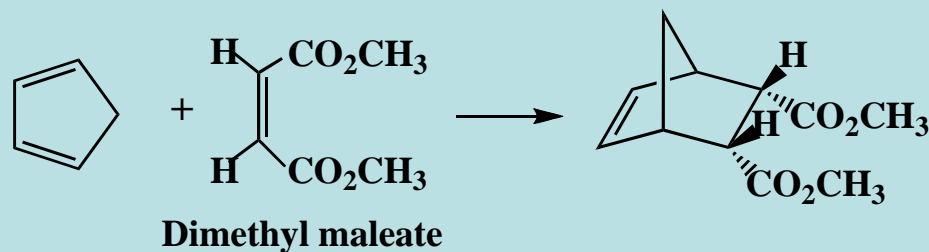
Exo and *endo* describe the stereochemistry of groups attached to bridged bicyclic ring systems. The **longest bridge** (excluding the one carrying the *exo* or *endo* group) is the **reference point**. Groups that project away from this bridge are in *exo* positions. Groups that project toward this bridge are in *endo* positions.

Example: a substituted bicyclo[2.2.1]heptane



The Endo Rule

The Diels-Alder reaction is **stereospecific** in regard to the configuration in the dienophile (***syn* addition**), and it is **stereoselective** in regard to the orientation of unsaturated groups of the dienophile relative to a cyclic diene.



Stereospecificity: CO₂CH₃ groups are *cis*

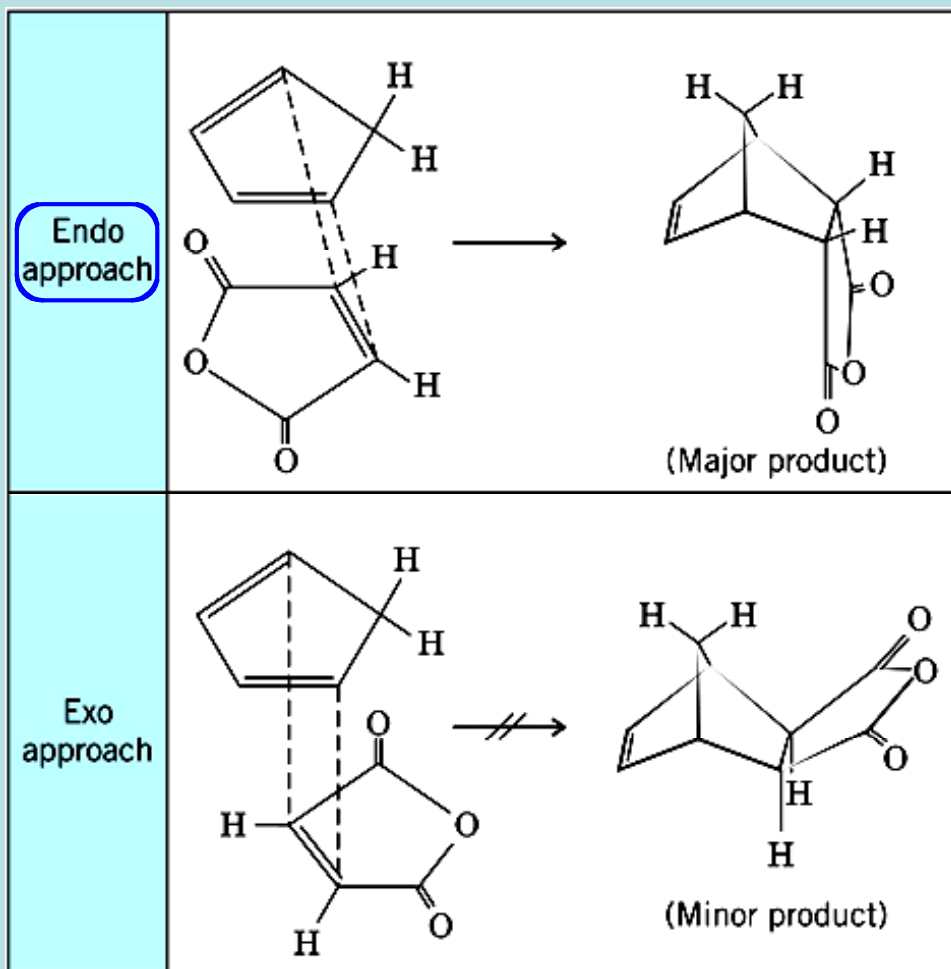
(In both reactant and product; if they had been *trans* in the reactant, they would have been *trans* in the product.)

Stereoselectivity: *endo* product is formed

(When, as in this case, the reaction is under kinetic control.)

Stereoselectivity in the Diels-Alder Reaction

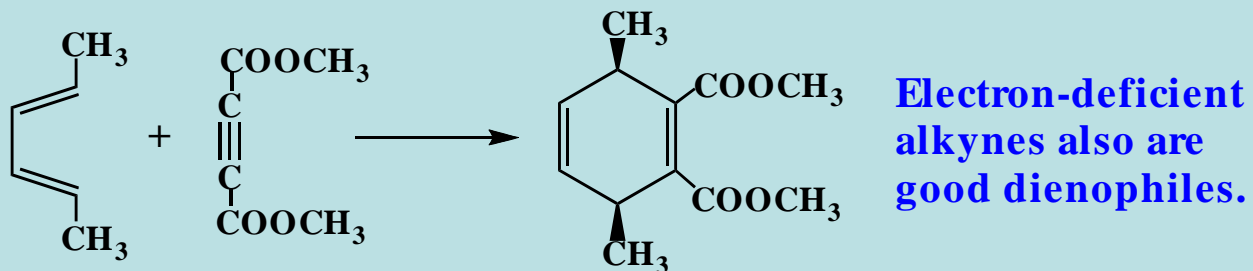
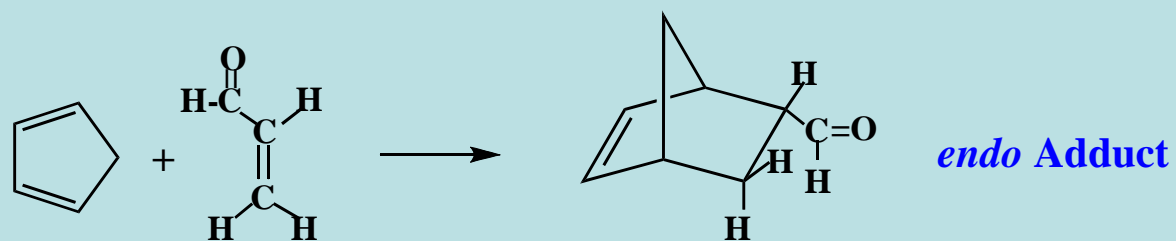
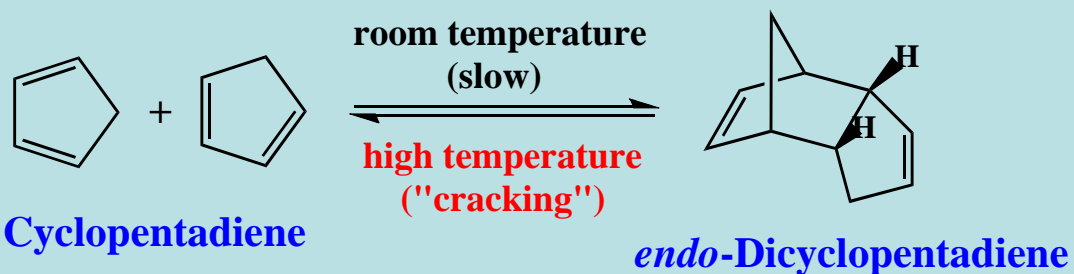
It is suggested that the diene and dienophile approach each other in **parallel planes**. The stereoselectivity arises because of the preference for the **endo approach**, which provides the more extensive π orbital overlap. This results in a lower ΔG^\ddagger for the creation of the *endo* adduct than for the *exo*.



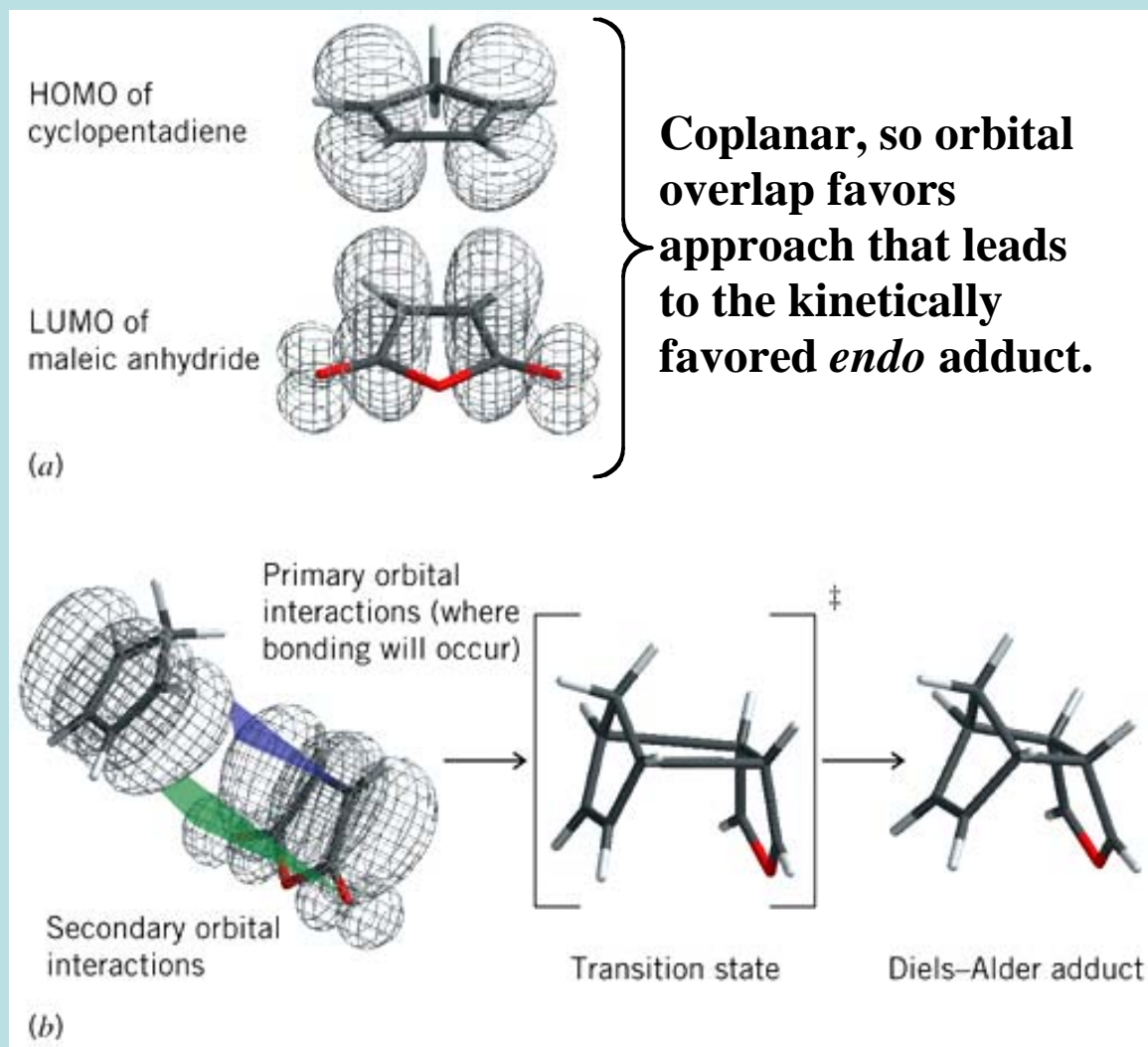
The *endo* adduct is formed more rapidly and is the major product.

Additional Diels-Alder Examples

The dimerization (and the **laboratory preparation**) of cyclopentadiene:



Molecular Orbital Picture of the Diels-Alder Reaction

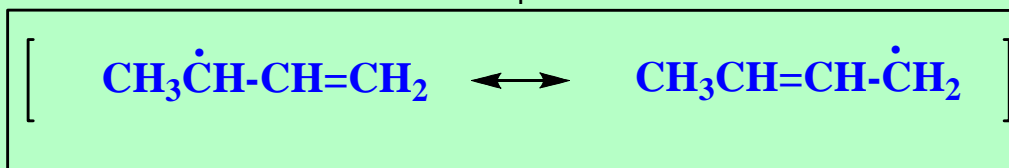
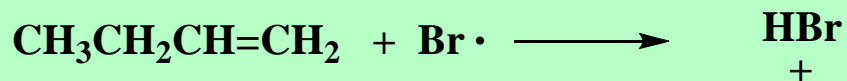


Interaction of the orbitals that lead to the new C-C σ bonds of the adduct are shown in purple, and interaction of the orbitals that guide the reactants into the *endo* mode are shown in green.

Quiz 13.01

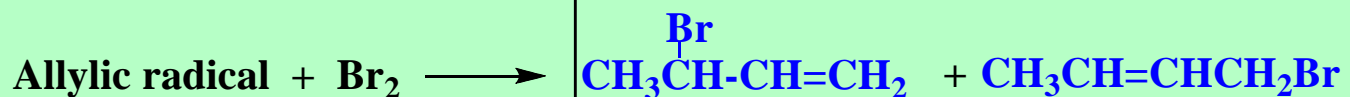
Draw the resonance structures of the allylic radical produced in the reaction of 1-butene and bromine radical:

(ignore *cis-trans* isomerism)



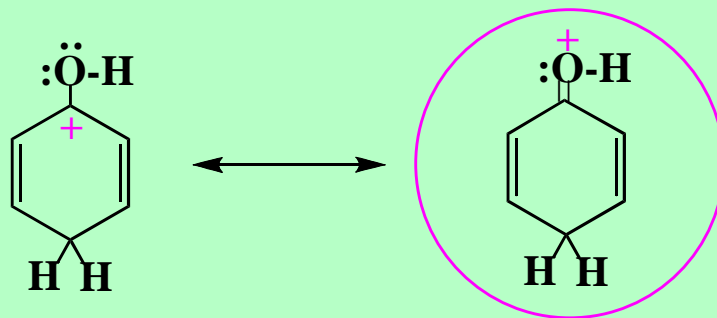
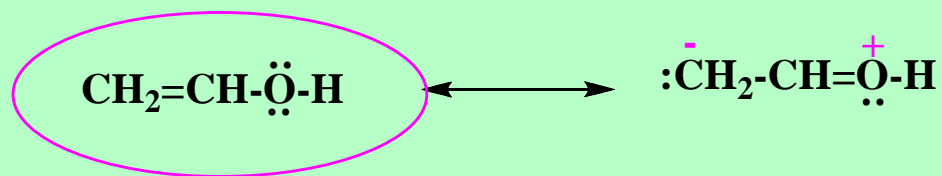
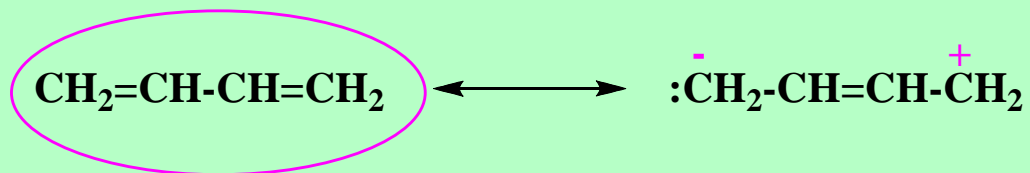
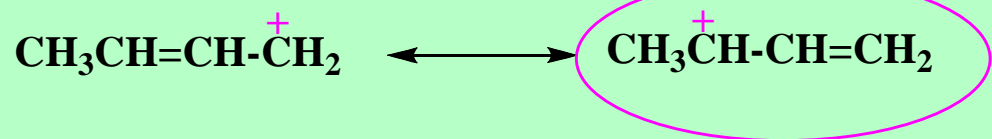
Provide the structures of the products from the reaction of the allylic radical intermediate with Br_2 .

(ignore *cis-trans* isomerism)



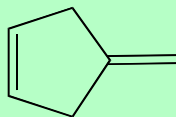
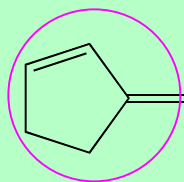
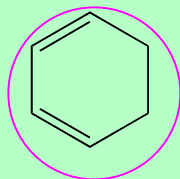
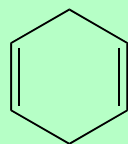
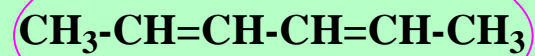
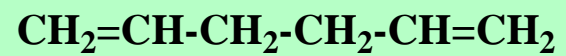
Quiz 13.02

For each pair of resonance structures below, circle the one that will make the larger contribution to the hybrid.



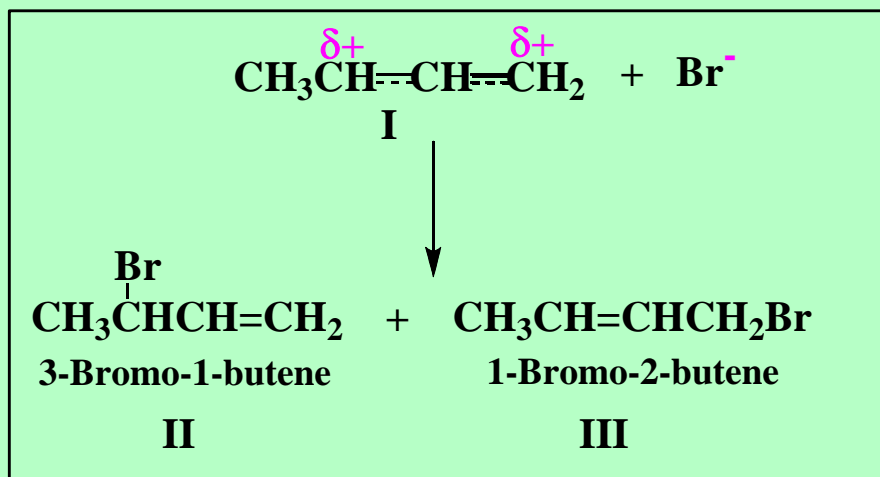
Quiz 13.03

Circle the more stable diene in each pair below.



Quiz 13.06

Complete the statements below about the reaction of the allylic cation I with bromide ion to give II and III.



The more stable product is III.

Under conditions of thermodynamic control, the major product is III.

At low temperature, the major product is II when product formation is under kinetic control.

When the reaction conditions allow the products to rapidly interconvert, product formation is under thermodynamic control.

Quiz 13.07

What dienophile and diene are required to produce the compound below?

