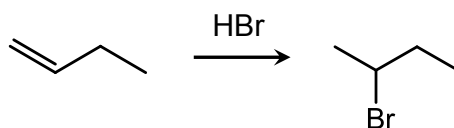


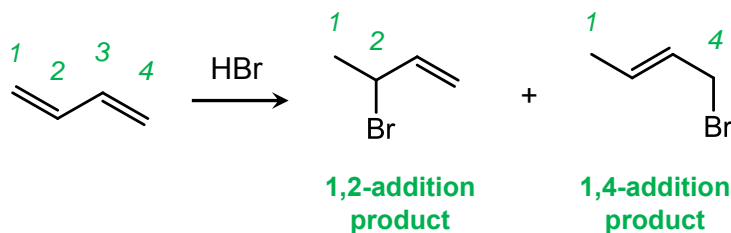
# 1,2- and 1,4 Addition to Dienes Pass Through Allyl Cation Intermediate

From CHEM 2301:

Hydrohalogenation  
of alkenes  
(Markovnikov  
addition)



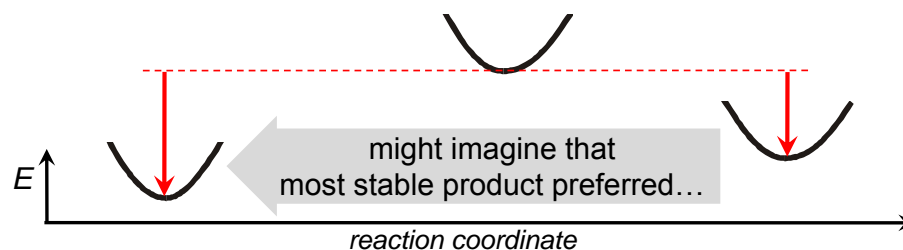
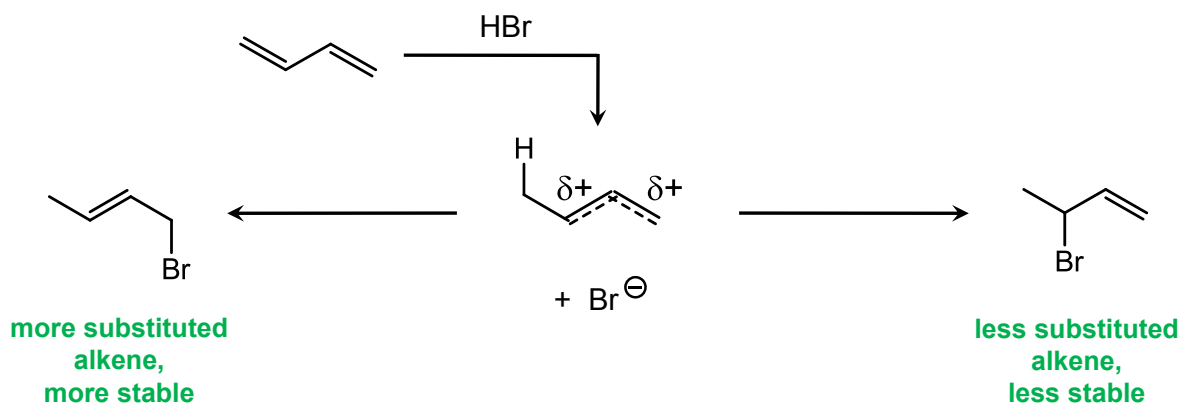
With a diene:



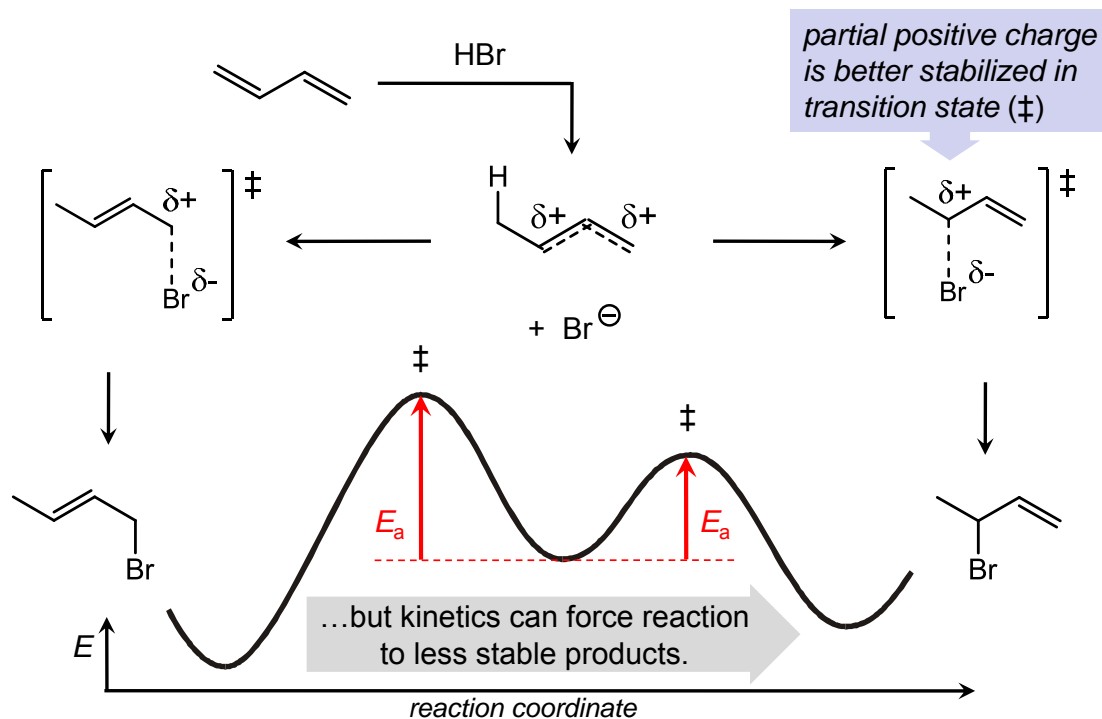
Which product is favored?

*Depends on reaction conditions.*

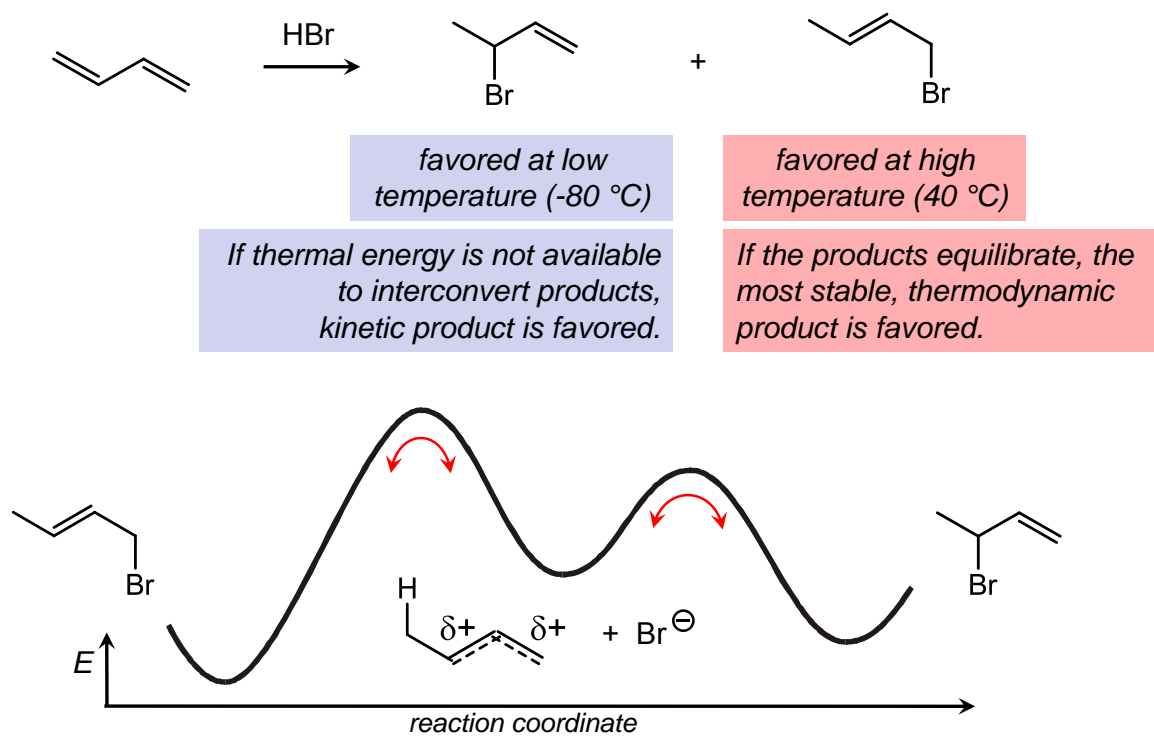
## Kinetic vs. Thermodynamic Control in Diene Additions



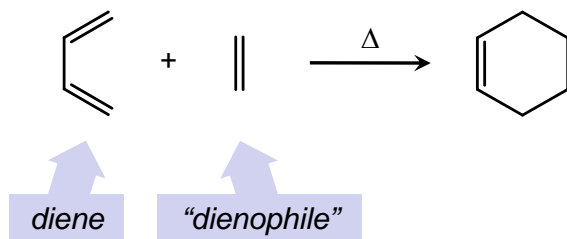
## Kinetic vs. Thermodynamic Control



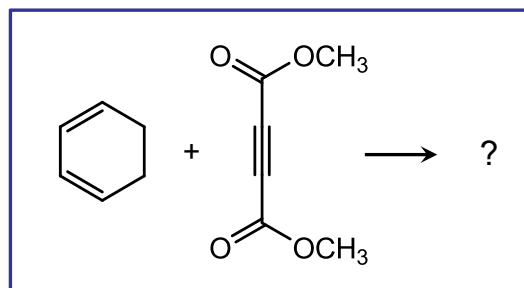
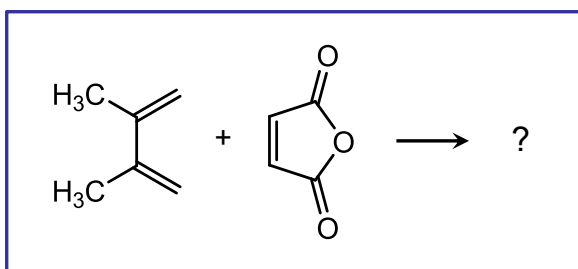
## Kinetic vs. Thermodynamic Control



# The Diels-Alder Reaction: A [4 + 2] Cycloaddition

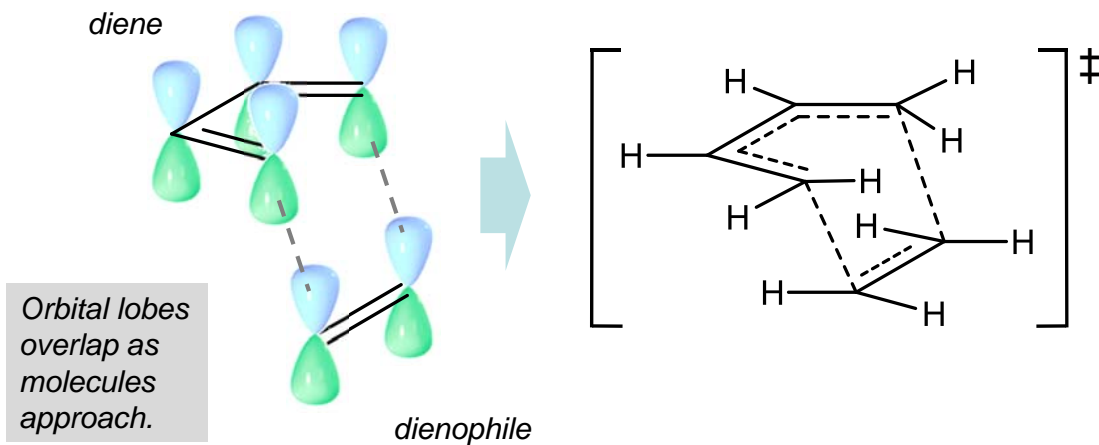


Examples:



*Dienophile can be an alkyne, but diene cannot.*

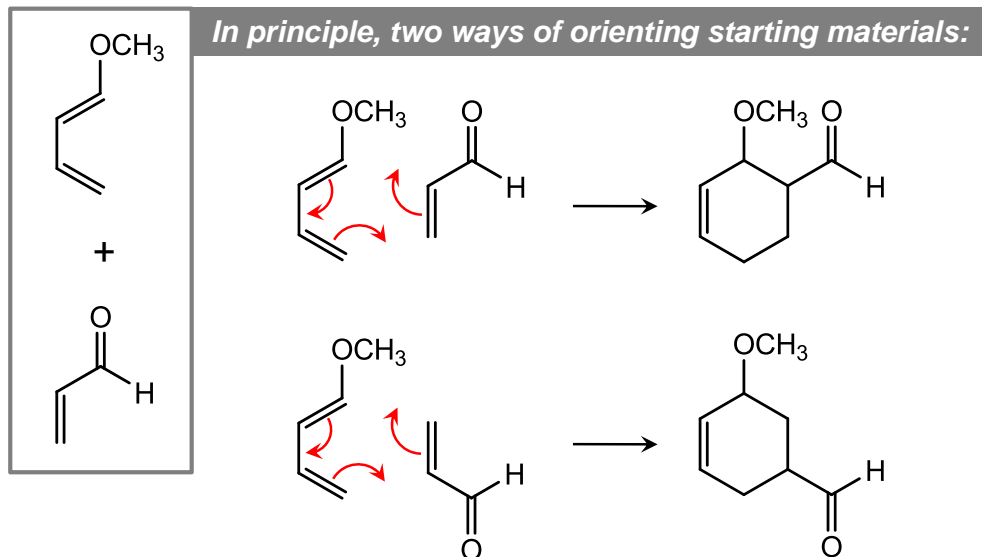
## The Diels-Alder Transition State Is Stabilized By Orbital Interactions



*So, diene and dienophile approach one another face-to-face.*

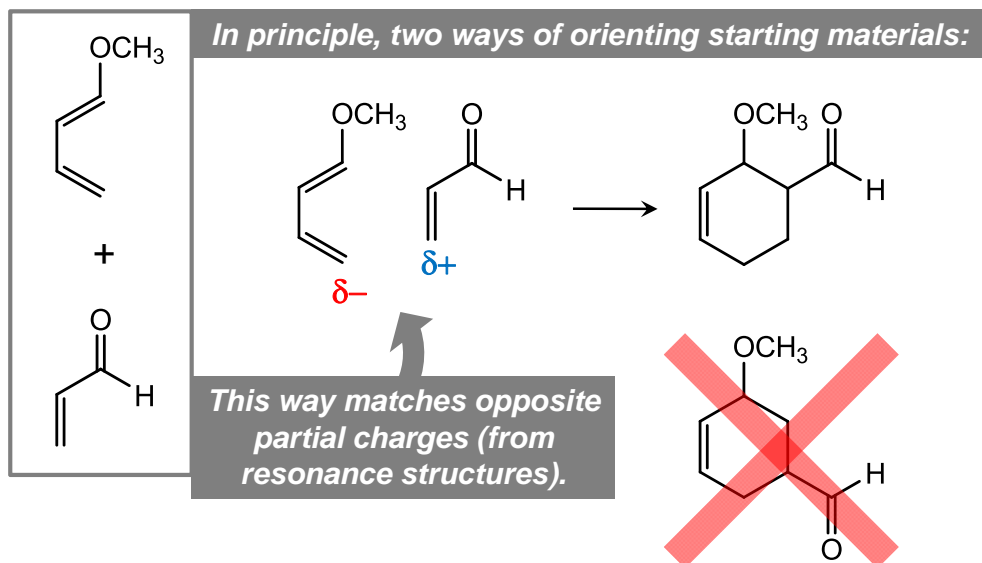
# What Factors Determine the Outcome of the Diels-Alder Reaction?

1. **Electron-donating/-withdrawing groups** affect success and regiochemistry.



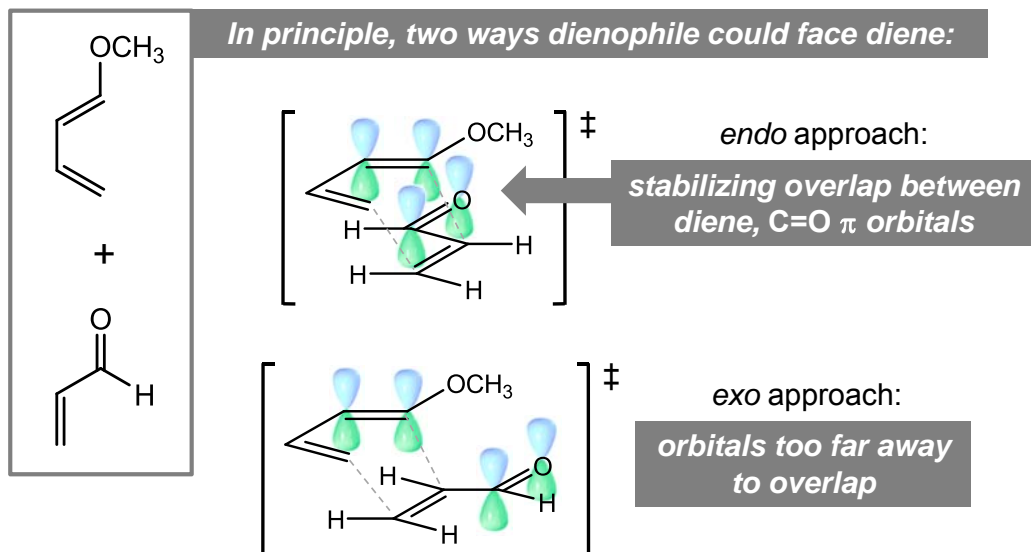
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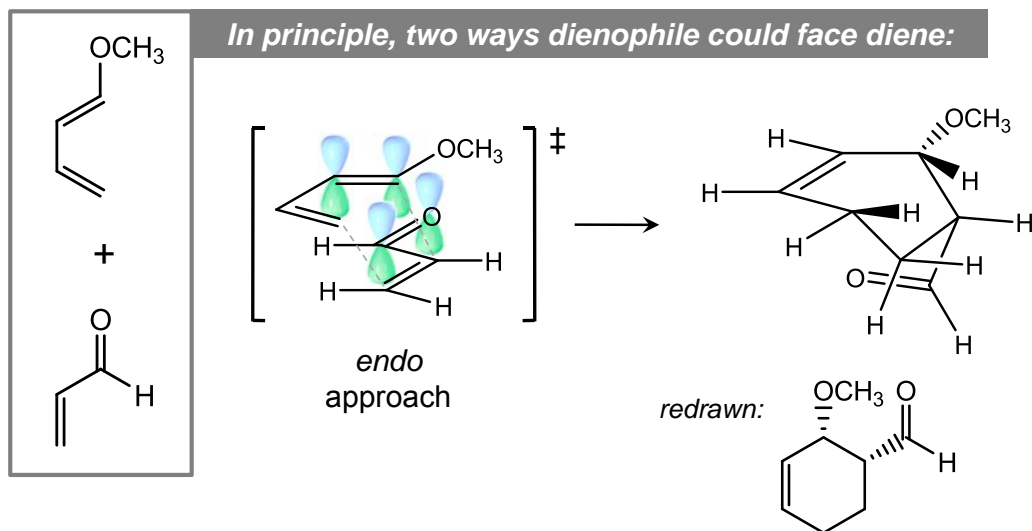
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2.  $\pi$  substituent on dienophile affects stereochemistry (by directing *endo* approach).



# What Factors Determine the Outcome of the Diels-Alder Reaction?

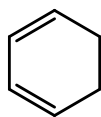
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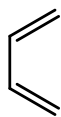
Approach from top face gives other enantiomer.

## What Factors Determine the Outcome of the Diels-Alder Reaction?

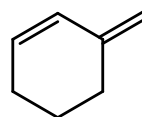
3. Diene must be in *s-cis* conformation to react. So, **forced *s-cis* conformation** helps.



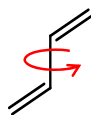
**very reactive**



**less reactive**  
(ordinarily in *s-trans* conformation)



**unreactive**  
(cannot assume *s-cis* conformation)



## What Factors Determine the Outcome of the Diels-Alder Reaction?

4. **Steric hindrance** in transition state can influence stereo- and regio-chemistry (but less than  $\pi$  interactions).

