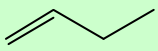
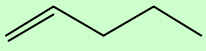
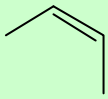
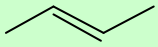
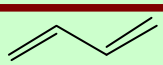
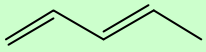
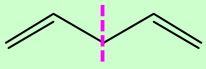
Conjugated Systems & Pericyclic Reactions

Conjugated Dienes

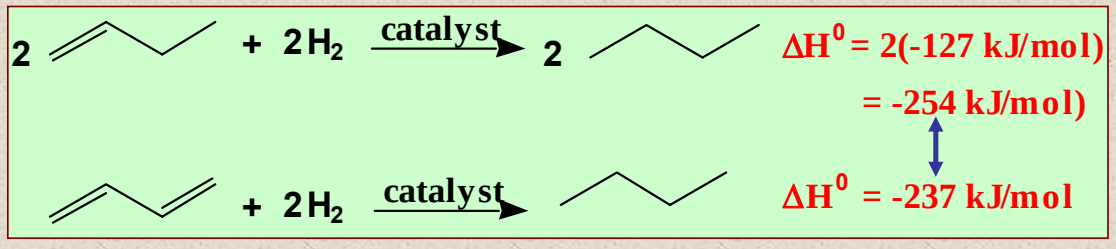
from heats of hydrogenation-relative stabilities of conjugated vs unconjugated dienes can be studied:

Name	Structural Formula	ΔH^0 kJ (kcal)/mol
1-Butene		-127 (-30.3)
1-Pentene		-126 (-30.1)
cis-2-Butene		-120 (-28.6)
trans-2-Butene		-115 (-27.6)
1,3-Butadiene		-237 (-56.5)
trans-1,3-Pentadiene		-226 (-54.1)
1,4-Pentadiene		-254 (-60.8)

conjugated

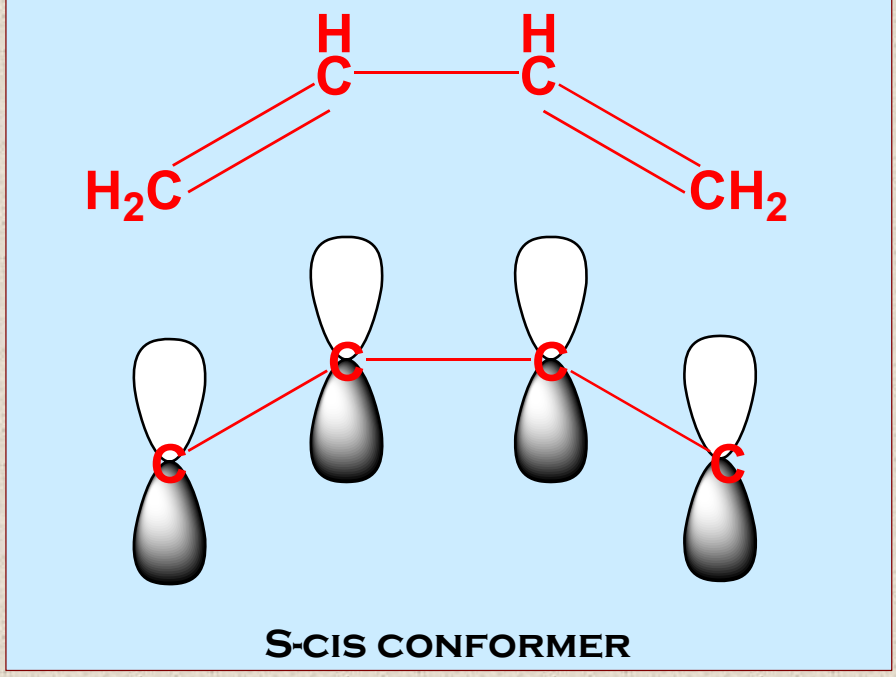
Conjugated Dienes

conjugation of the double bonds in 1,3-butadiene gives an extra stability of approximately 17 kJ (4.1 kcal)/mol



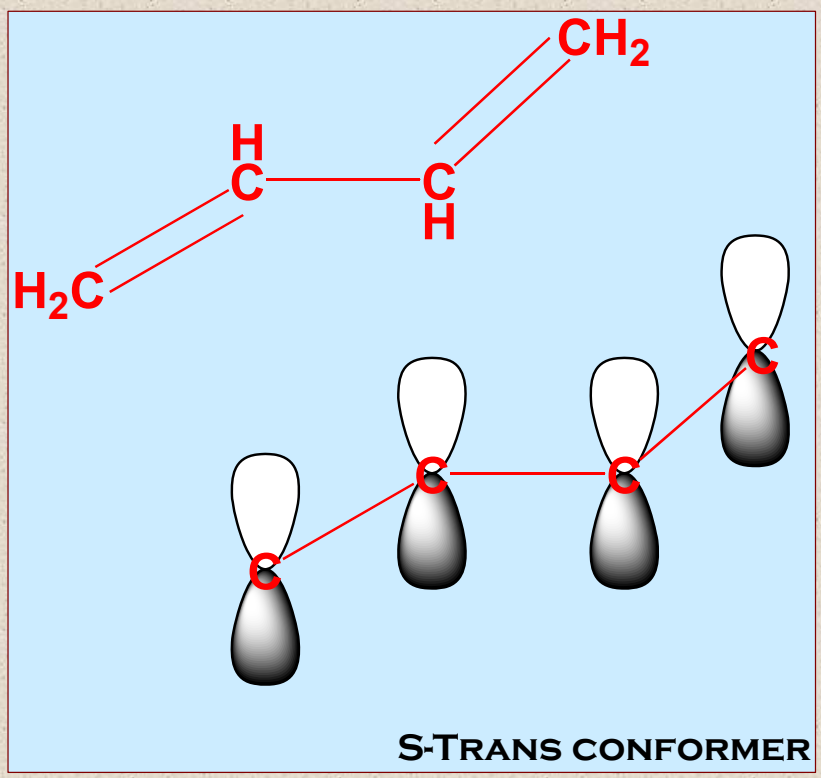
Conjugated Dienes

THE π SYSTEMS OF THE 2 OLEFINS OVERLAP



S-CIS CONFORMER

Conjugated Dienes



Summary of C—C Bond Reactions

Nucleophilic displacement of a leaving group by "R $^-$"

- Gilman & Grignard additions
- Alkyne and $^-$CN anions
- Alkylation of enolates
- Alkylation of enamines

Nucleophilic addition To carbonyl & carboxyl groups

- Gilman, Grignard & organolithium
- Alkyne and CN anions
- Aldol reactions
- Claisen & Dieckmann
- Enamine acylations
- Wittig & variations

Conjugate addition to α,β- unsaturated carbonyls

- Michael reaction

Carbene / carbenoid additions

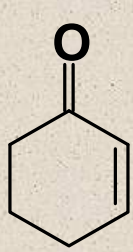
- Simmons-Smith
- cyclopropanations

Electrophilic Aromatic Substitutions

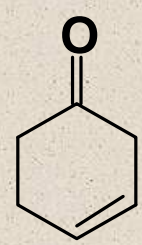
- Friedel Crafts alkylation & acylations
- Diazonium with CN

Conjugated Systems

– systems containing conjugated double bonds, not just those of dienes, are more stable than those containing unconjugated double bonds



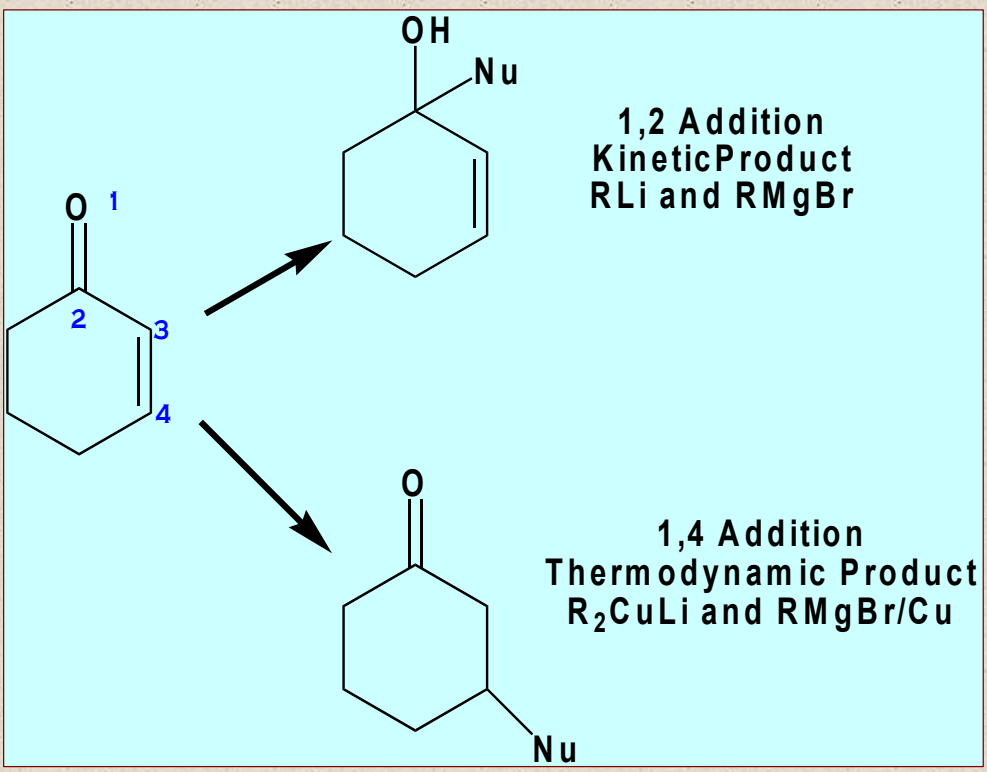
2-Cyclohexenone
(more stable)



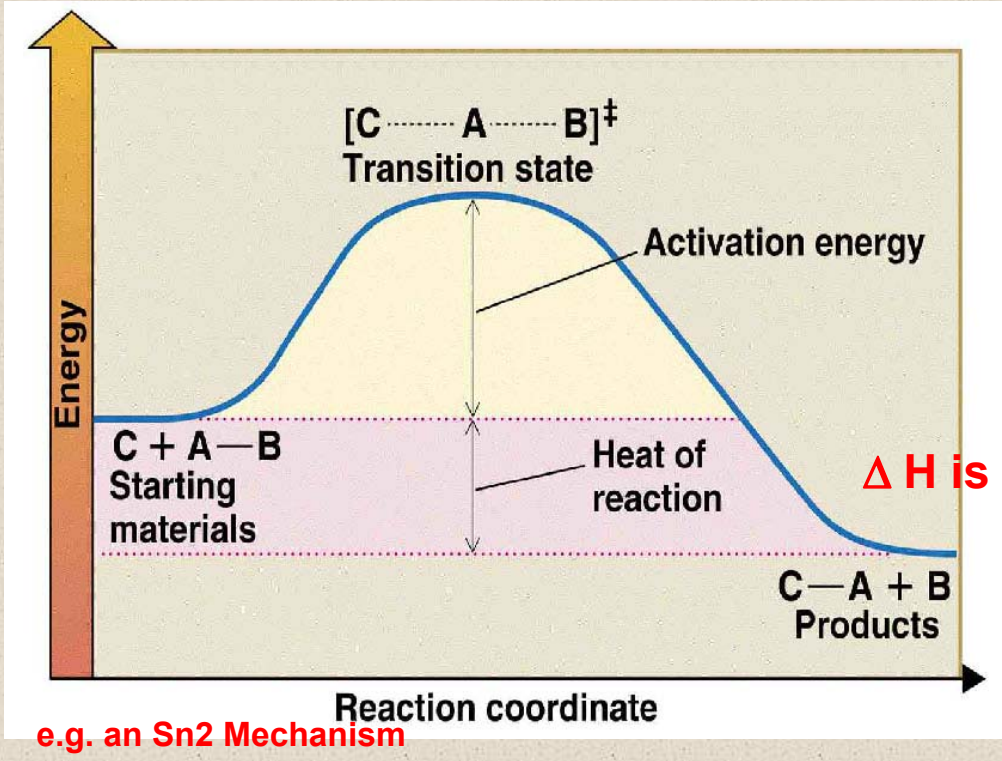
3-Cyclohexenone
(less stable)

Most significant are α,β-unsaturated carbonyl

1,2 vs 1,4-Addition



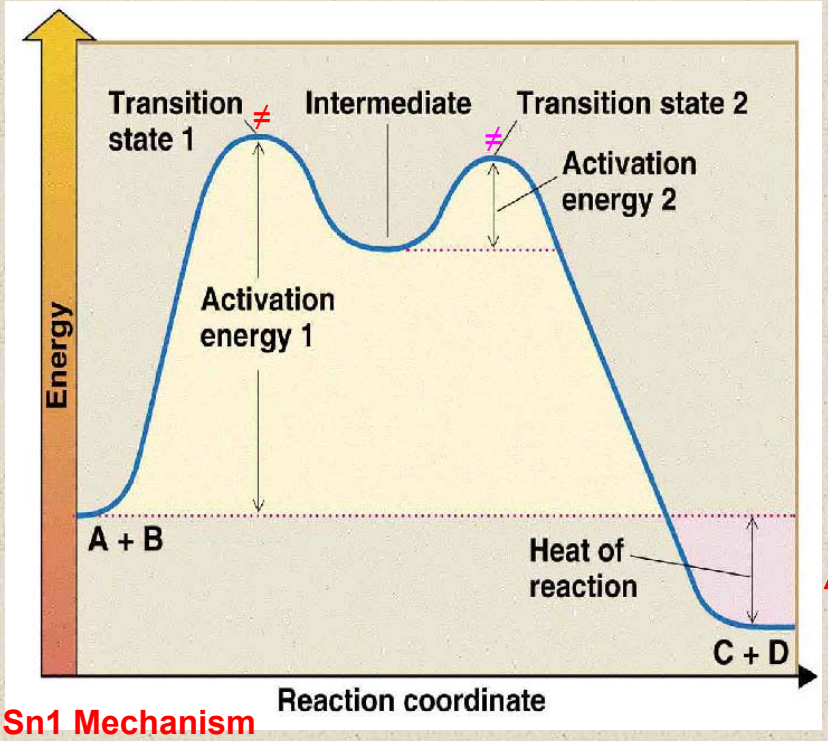
Simple Rxn Coordinate Diagram



Δ H is (-)

e.g. an Sn2 Mechanism

A Two Step Mechanism:

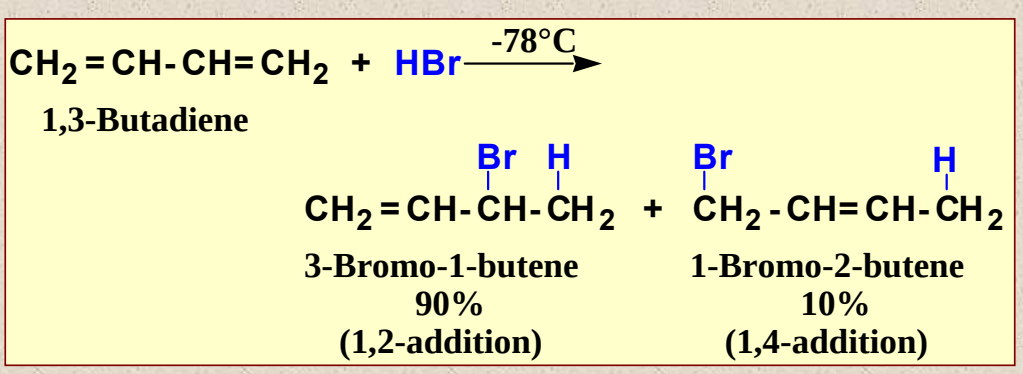


Δ H is (-)

e.g. an Sn1 Mechanism

1,2 vs 1,4-Addition

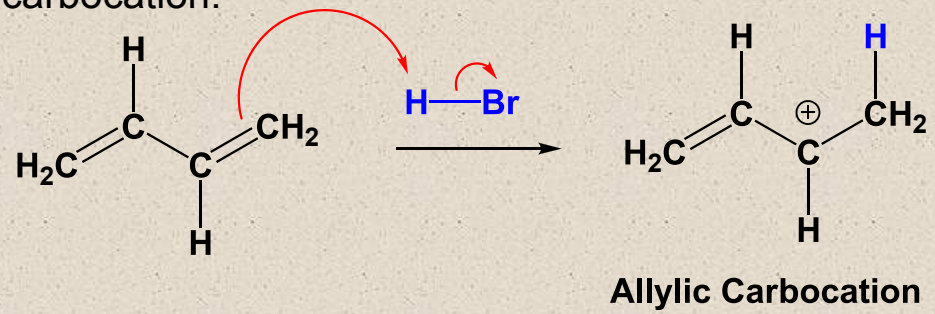
- Addition of 1 mol of HBr to butadiene at -78°C gives a mixture of two constitutional isomers:



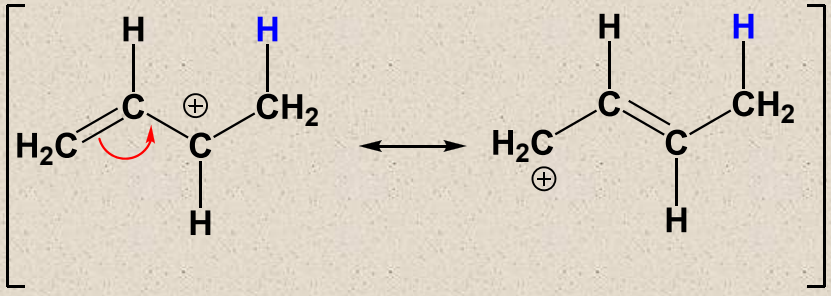
– these products can be explained by the following two-step mechanism

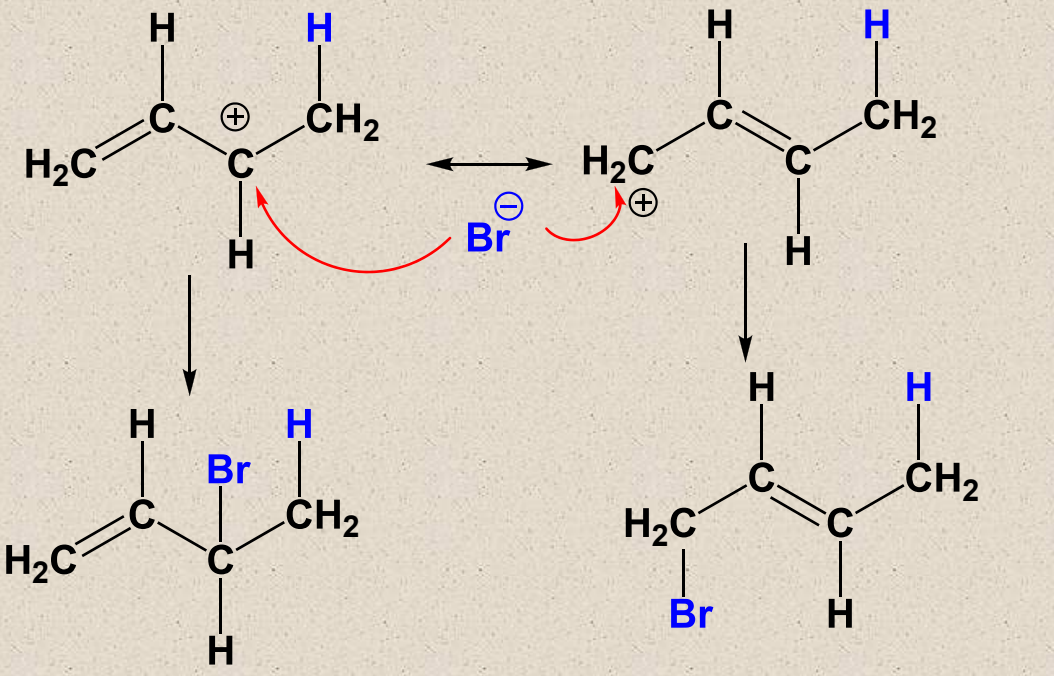
1,2- and 1,4-Addition

the key intermediate is a resonance-stabilized allylic carbocation:



Allylic Carbocation





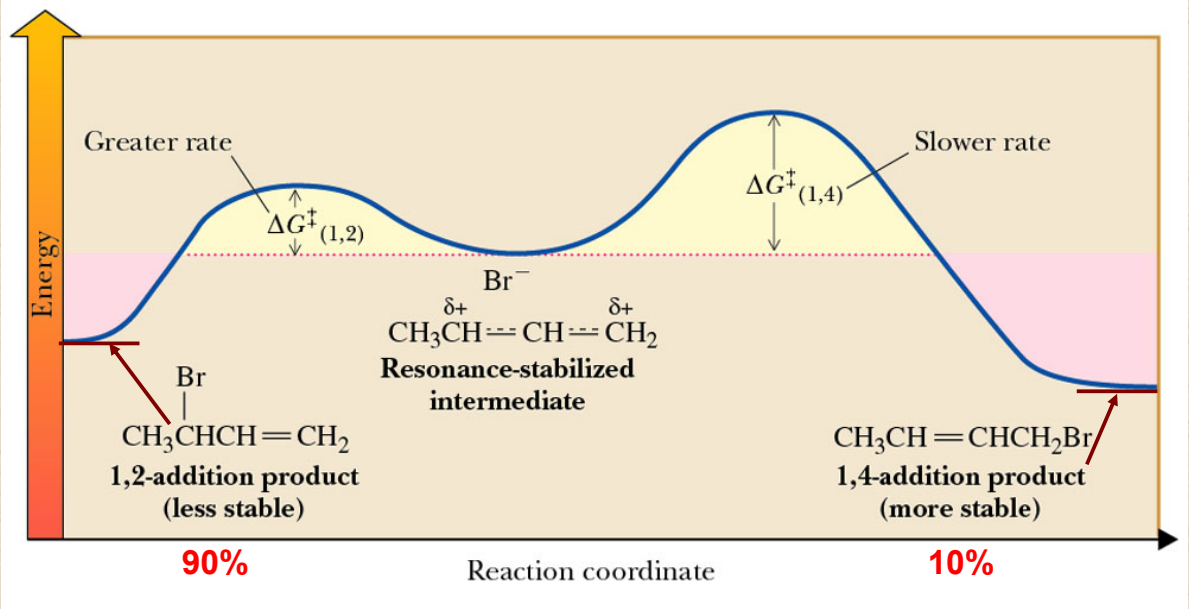
Less"stable"
1,2 adduct
(Monosubstituted DB)

90%

More "stable"
1,4 adduct
(Disubstituted DB)

10%

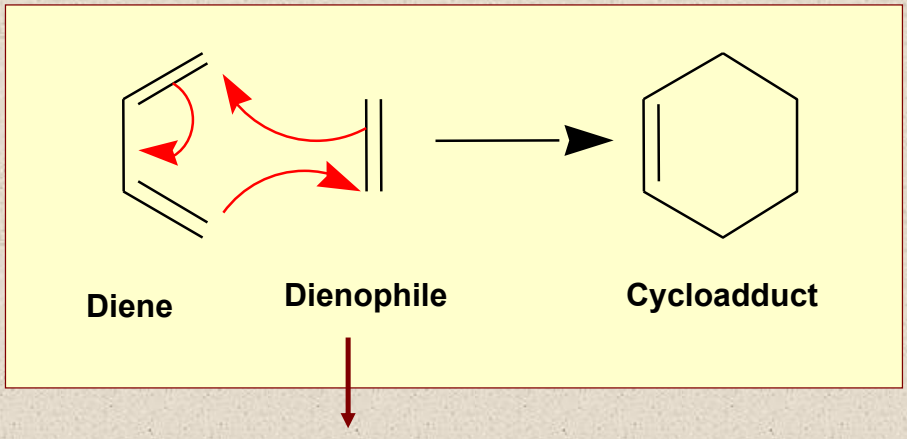
Kinetic vs Thermodynamic Control



$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$ Gibbs Free energy

For transition states: $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$

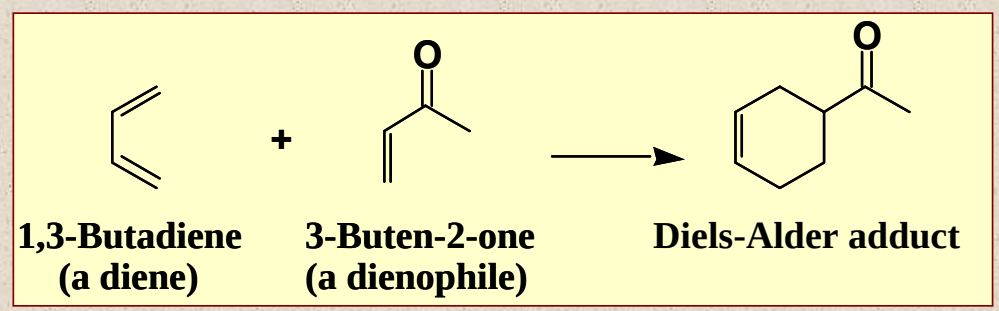
Diels-Alder Reaction



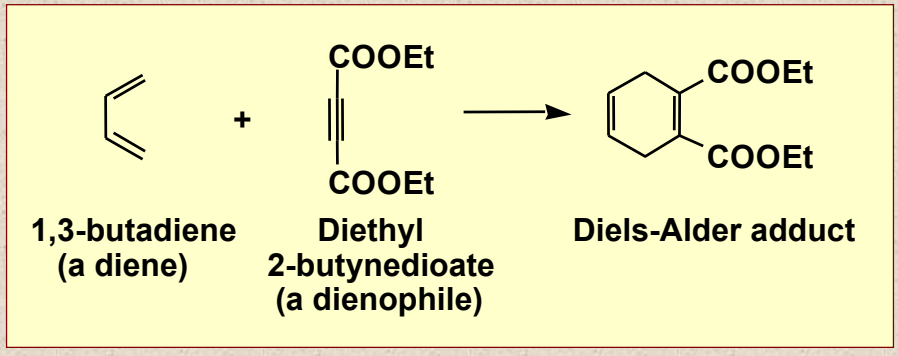
Dienophile is an alkene which is a reactant in the Diels-Alder reaction.

Diels-Alder Reaction

- Diels-Alder reaction: a cycloaddition reaction of a **conjugated diene** and certain types of double and triple bonds
  - **dienophile:** "diene-loving"
  - **Diels-Alder adduct:** the product of a Diels-Alder reaction

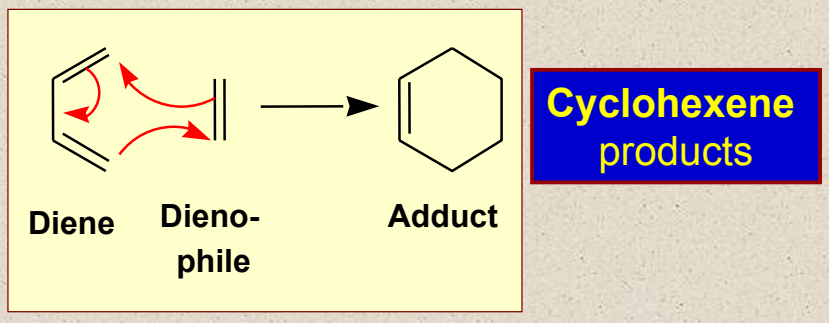


– alkynes also function as dienophiles



– **cycloaddition reaction:** a reaction in which two reactants add together in a single step to form a cyclic product

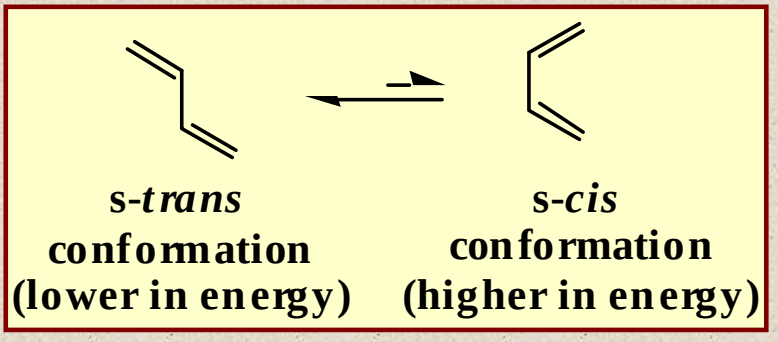
– the Diels-Alder reaction is shown in the following way:

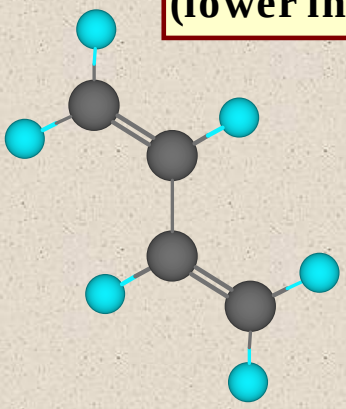


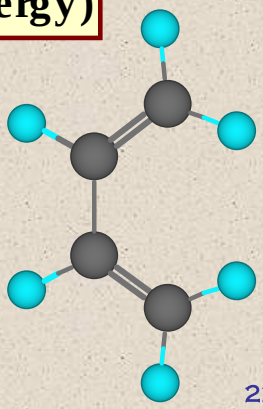
- **the special value of D-A reactions are that they**
  - **(1) form six-membered rings**
  - **(2) form 2 new C-C bonds at the same time**
  - **(3) are stereospecific and regioselective**

- **Mechanism**
  - no evidence for the participation of either radical or ionic intermediates
  - the Diels-Alder reaction is a *pericyclic reaction*
- **Pericyclic reaction:** a reaction that takes place in a single step, without intermediates, and involves a cyclic redistribution of bonding electrons

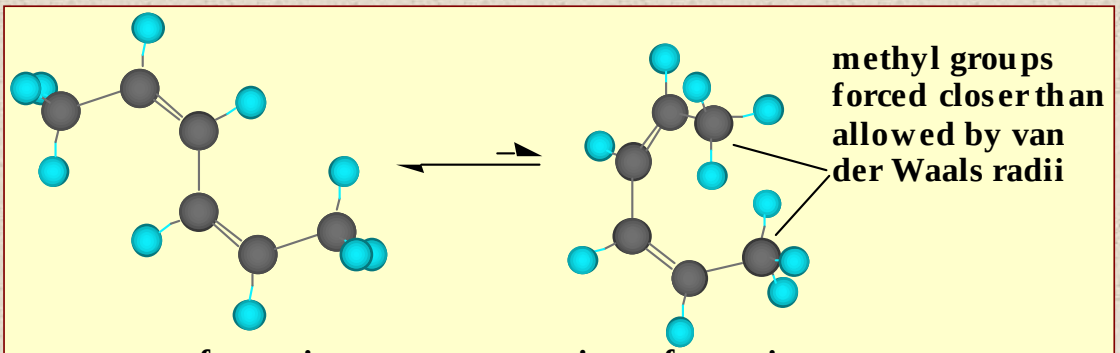
- the conformation of the diene must be s-*cis*



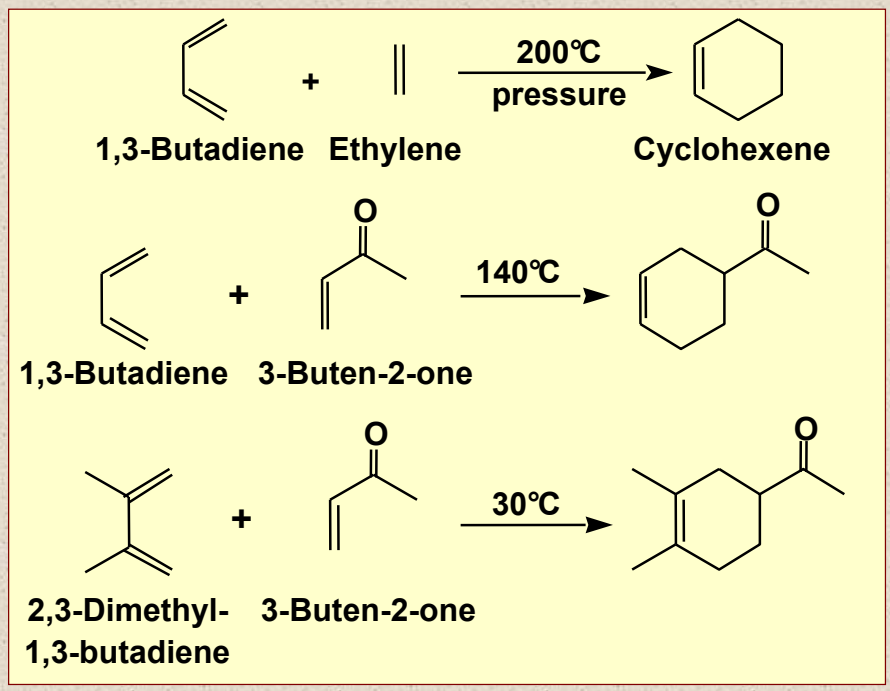




– (2*Z*,4*Z*)-2,4-hexadiene is unreactive in Diels-Alder reactions because nonbonded interactions prevent it from assuming the planar s-*cis* conformation



reaction is facilitated by a combination of electron-withdrawing substituents on the dienophile and electron-releasing substituents on the diene



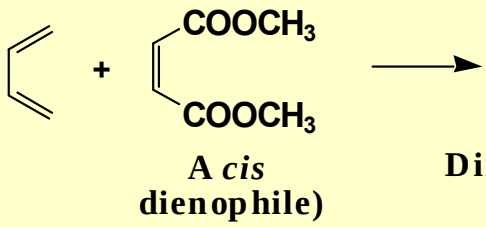
Electron-Releasing Groups	Electron-Withdrawing Groups
-CH_3, alkyl groups	-CHO (aldehyde, ketone)
-OR (ether)	-COOH (carboxyl)
-OOCR (ester)	-COOR (ester)
	-NO_2 (nitro)
	-C≡N (cyano)

Use these to activate the diene

Use these to activate the dienophile

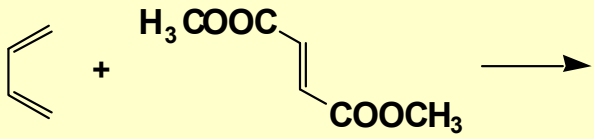
Stereochemistry of the Dienophile

the configuration of the dienophile is retained



A *cis* dienophile)

Dimethyl *cis*-4-cyclohexene-1,2-dicarboxylate



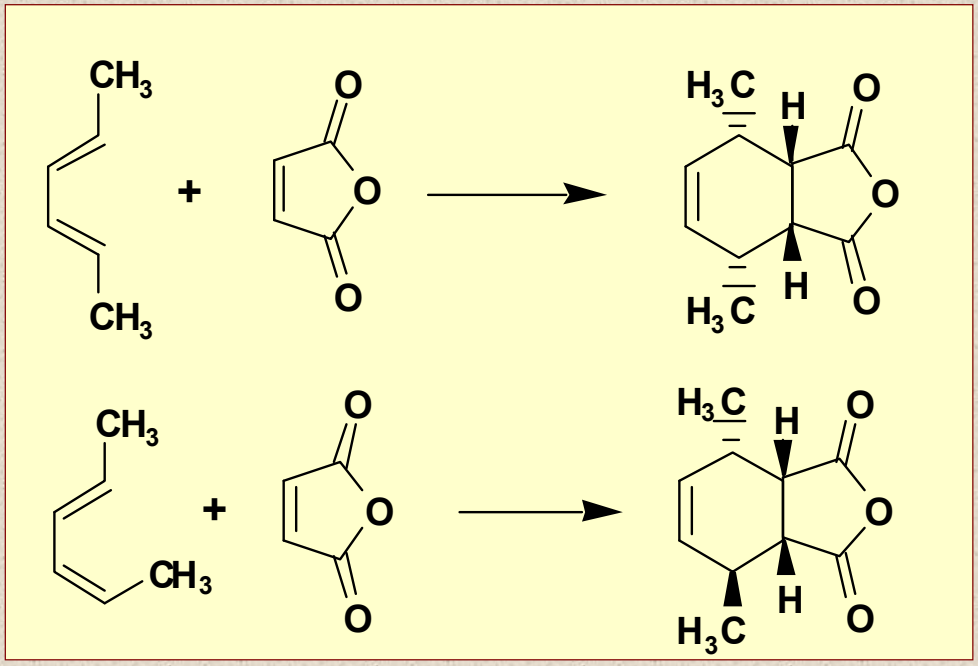
A *trans* dienophile)

Dimethyl *trans*-4-cyclohexene-1,2-dicarboxylate

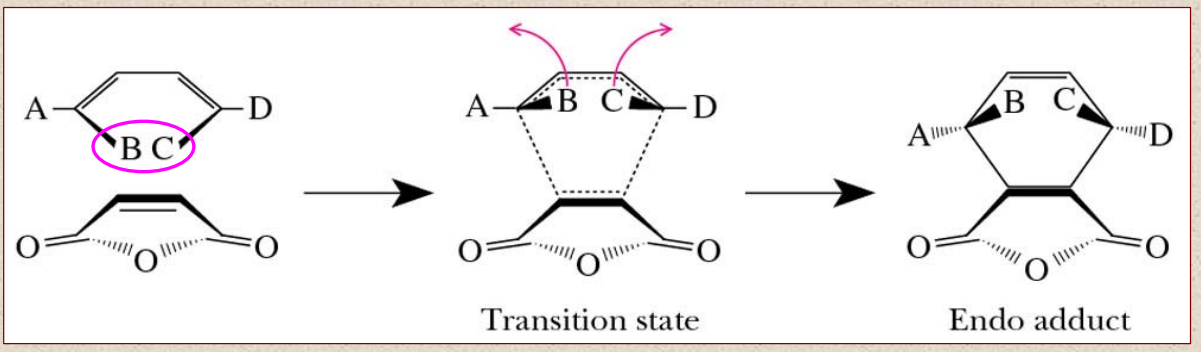
cis-alkene gives *cis* products

Stereochemistry of the Diene

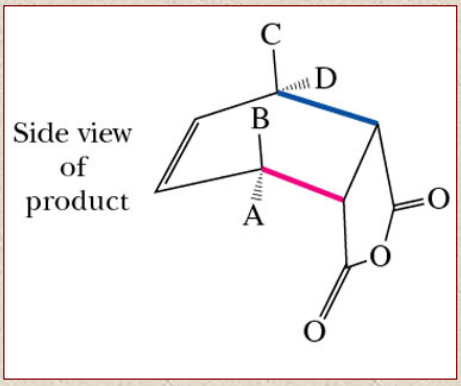
the configuration of the diene is retained:

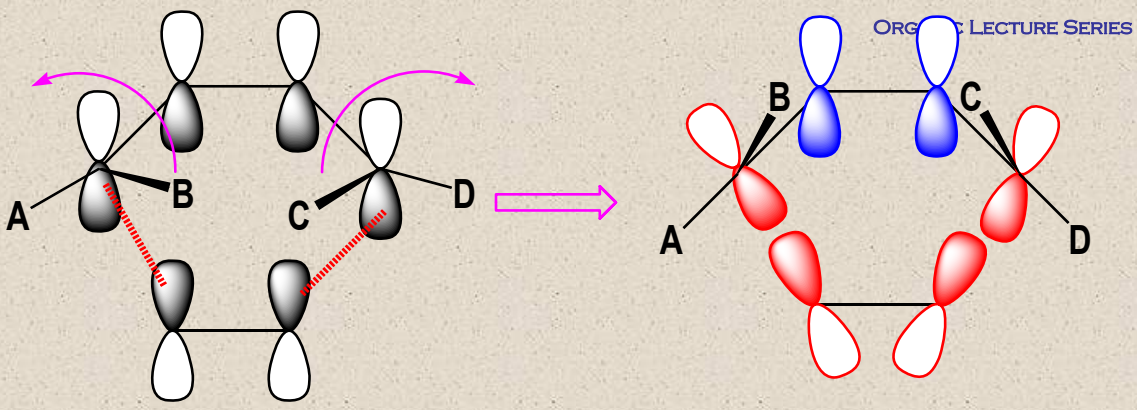


Stereochemistry of the Diene

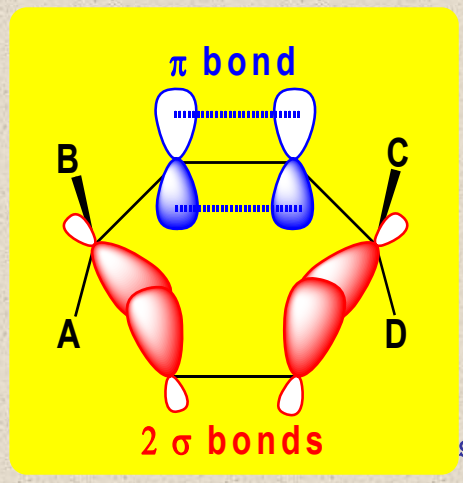


The diene's substitutents are turned "inside out"

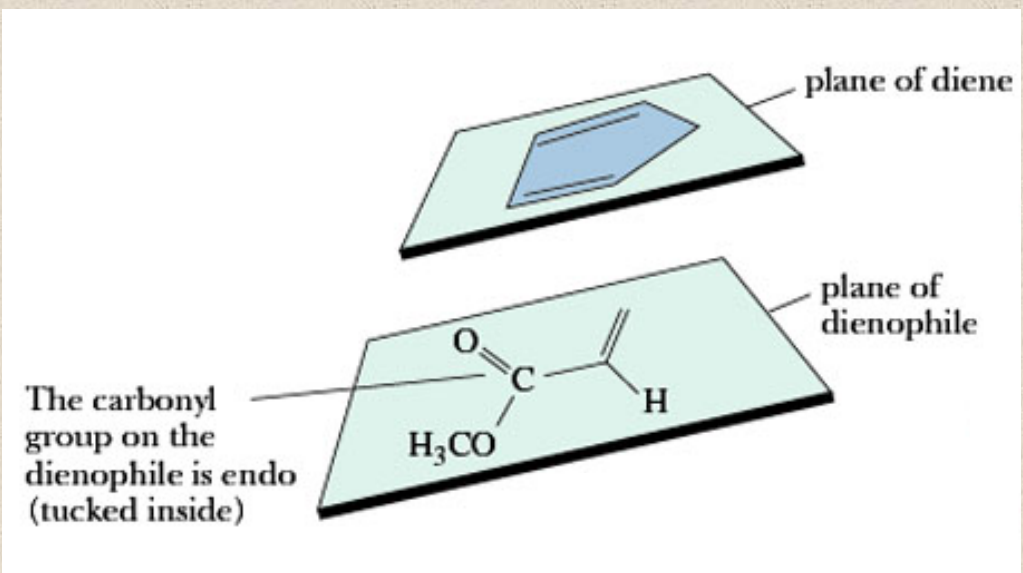




B rotates counterclockwise
C rotates clockwise
This is called:
Disrotation



Summary



Summary

1. New bonds form
2. Envelope flap moves up
3. H moves to exo position; $-CO_2CH_3$ moves to endo position