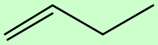
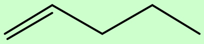
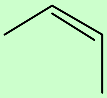
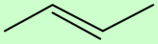
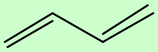
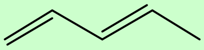
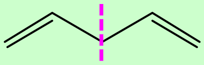
Conjugated Systems & Pericyclic Reactions

Conjugated Dienes

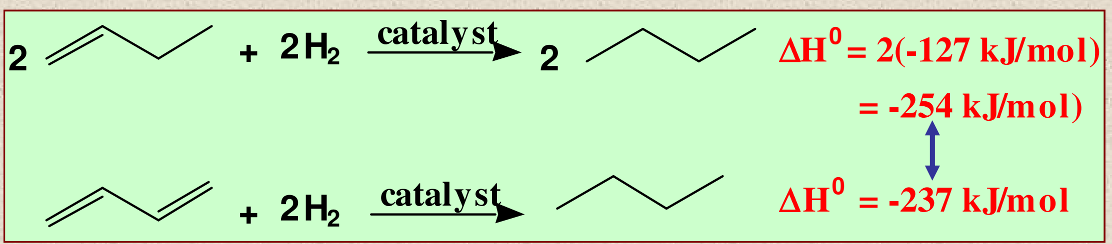
from heats of hydrogenation-relative stabilities of conjugated vs unconjugated dienes can be studied:

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

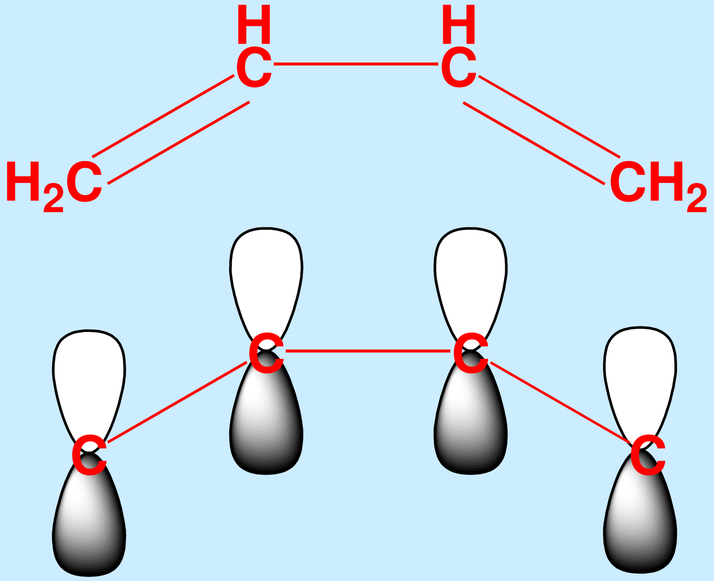


$\Delta H^0 = 2(-127 \text{ kJ/mol}) = -254 \text{ kJ/mol})$

$\Delta H^0 = -237 \text{ kJ/mol}$

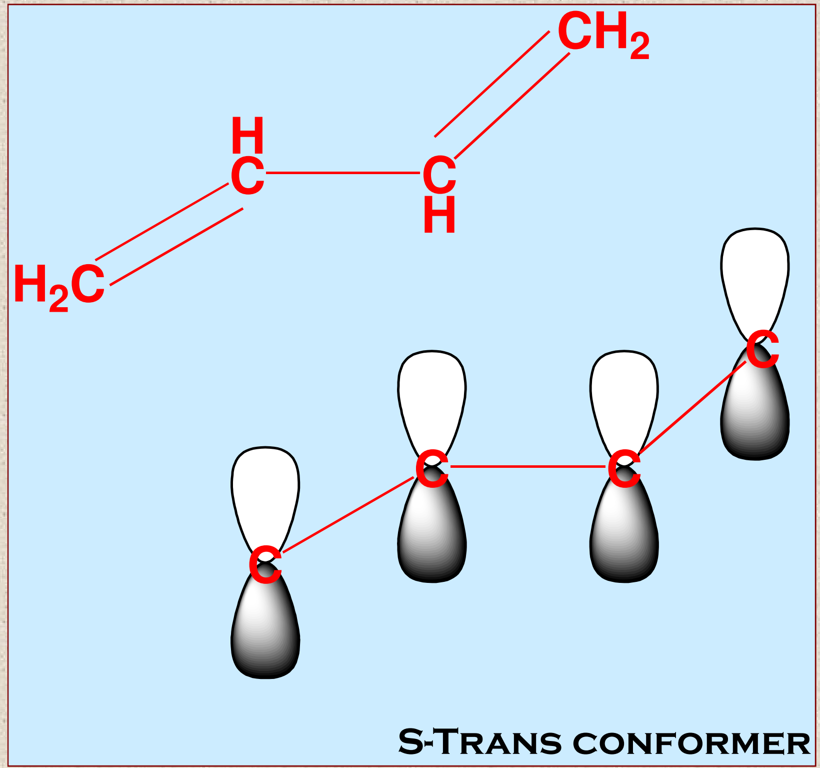
Conjugated Dienes

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

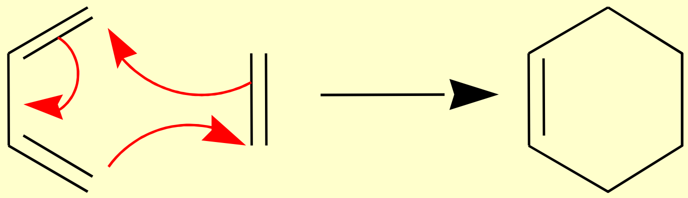
Carbene / carbenoid additions

- Simmons-Smith
- cyclopropanations

Electrophilic Aromatic Substitutions

- Friedel Crafts alkylation & acylations
- Diazonium with CN

Diels-Alder Reaction

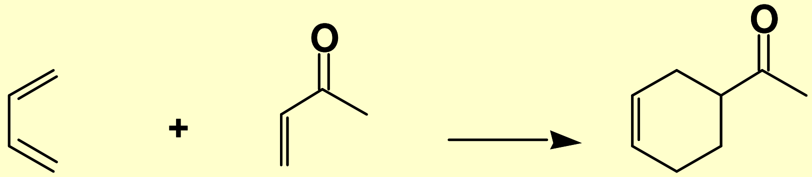


Diene **Dienophile** **Cycloadduct**

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

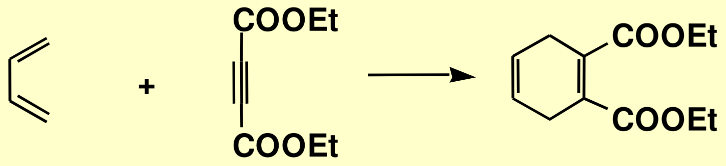
Diels-Alder Reaction

- 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



1,3-Butadiene (a diene) **3-Buten-2-one (a dienophile)** **Diels-Alder adduct**

– alkynes also function as dienophiles



1,3-butadiene (a diene)

Diethyl 2-butynedioate (a dienophile)

Diels-Alder adduct

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

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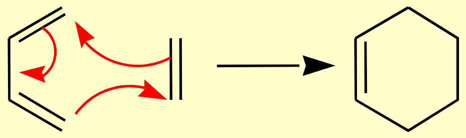
– the Diels-Alder reaction is shown in the following way:



Diene **Dieno-phile** **Adduct**

Cyclohexene products

- **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

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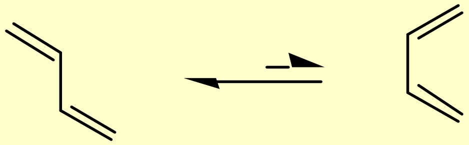
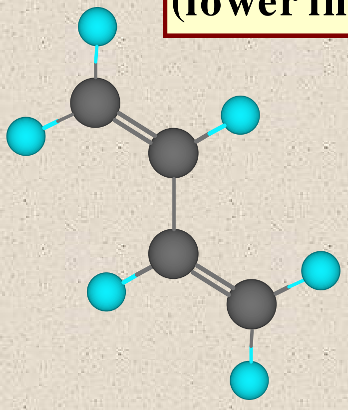
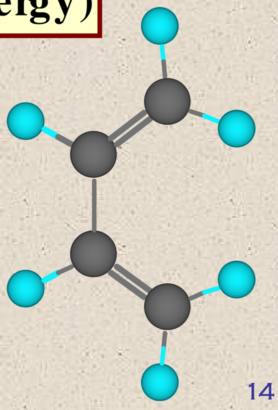
- the conformation of the diene must be s-*cis*



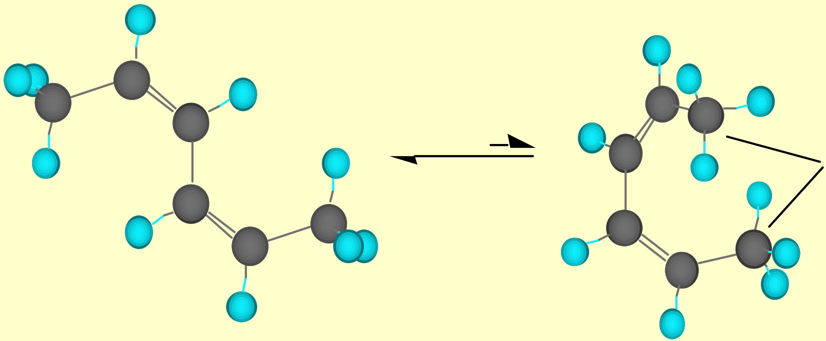
s-*trans* conformation (lower in energy)

s-*cis* conformation (higher in energy)





– (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



methyl groups forced closer than allowed by van der Waals radii

s-*trans* conformation (lower energy)

s-*cis* conformation (higher energy)

(2Z,4Z)-2,4-Hexadiene

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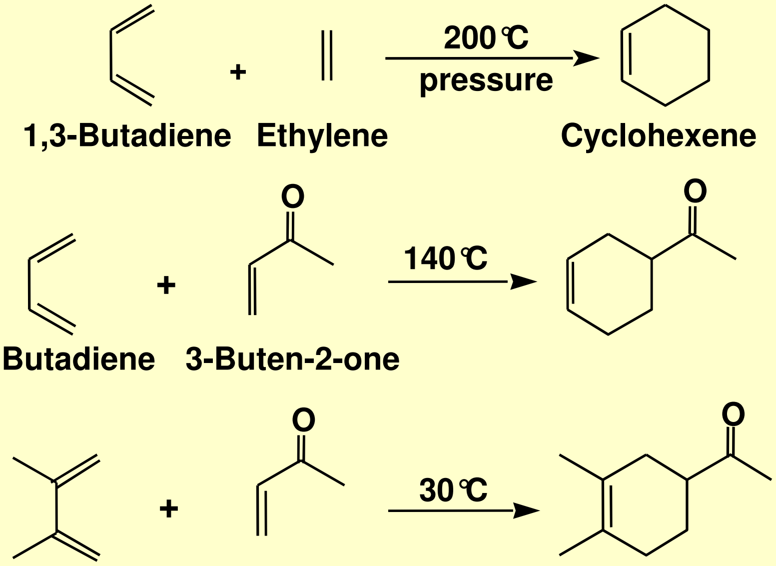
reaction is facilitated by a combination of electron-withdrawing substituents on the dienophile and electron-releasing substituents on the diene



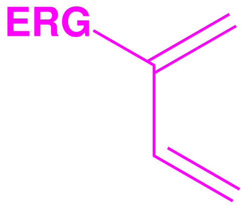
1,3-Butadiene + **Ethylene** → **Cyclohexene**

1,3-Butadiene + **3-Buten-2-one**

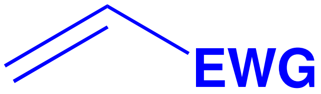
2,3-Dimethyl-1,3-butadiene + **3-Buten-2-one**

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

Use these to activate the diene

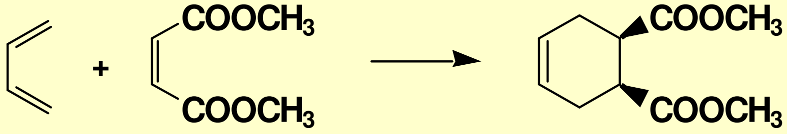


Use these to activate the dienophile



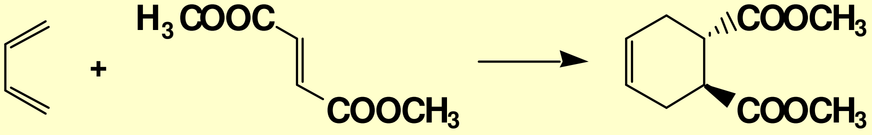
Stereochemistry of the Dienophile

the configuration of the dienophile is retained



A *cis* dienophile)

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



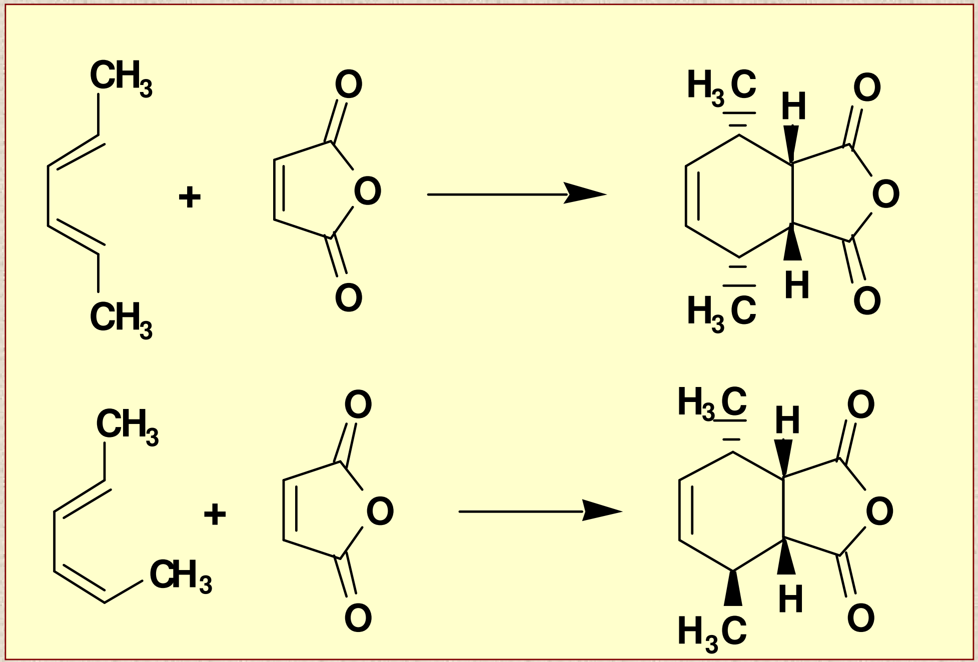
A *trans* dienophile)

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

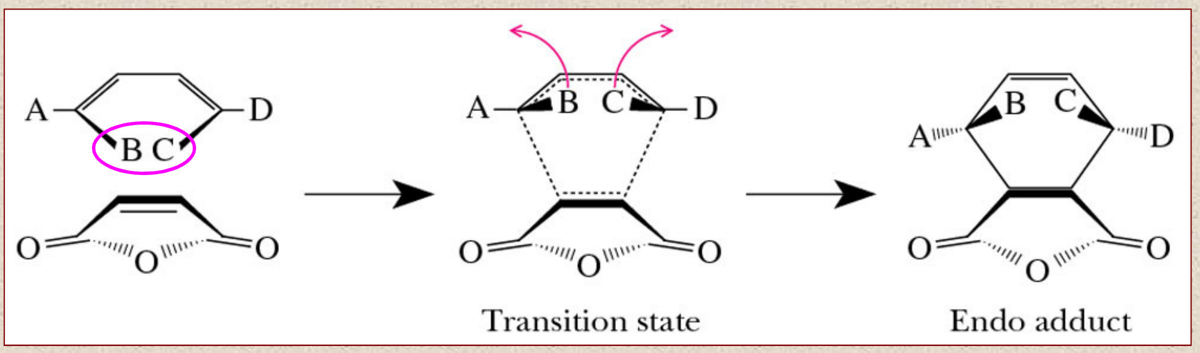
cis-alkene gives *cis* products

Stereochemistry of the Diene

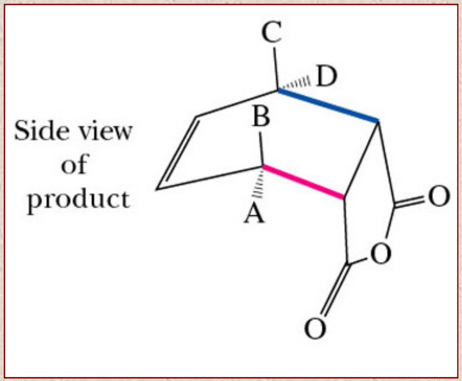
the configuration of the diene is retained:

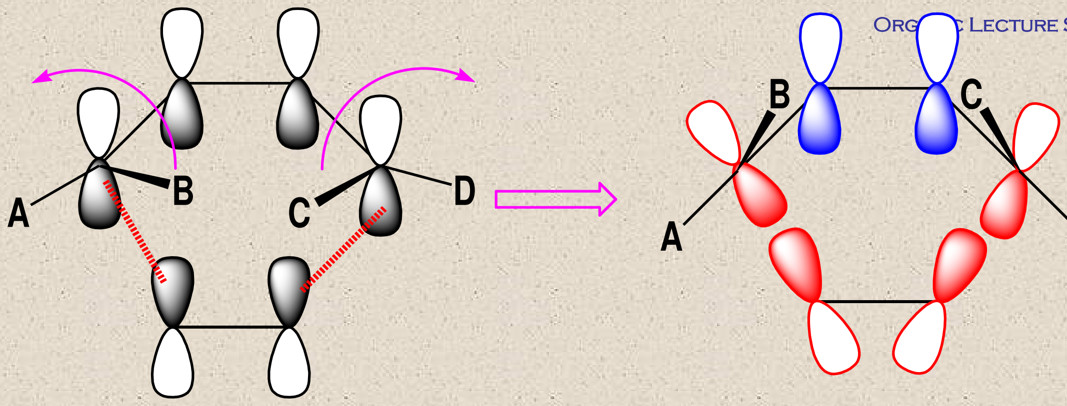


Stereochemistry of the Diene

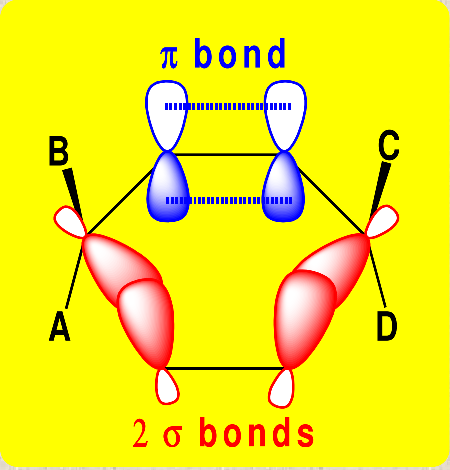


The diene's substitutents are turned "inside out"

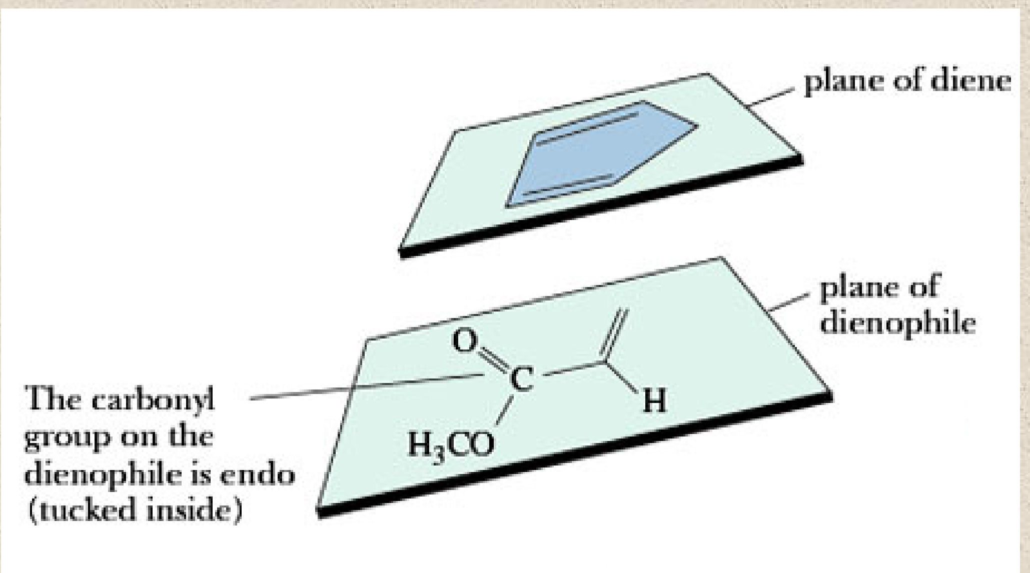




B rotates counterclockwise
C rotates clockwise
This is called:
Disrotation

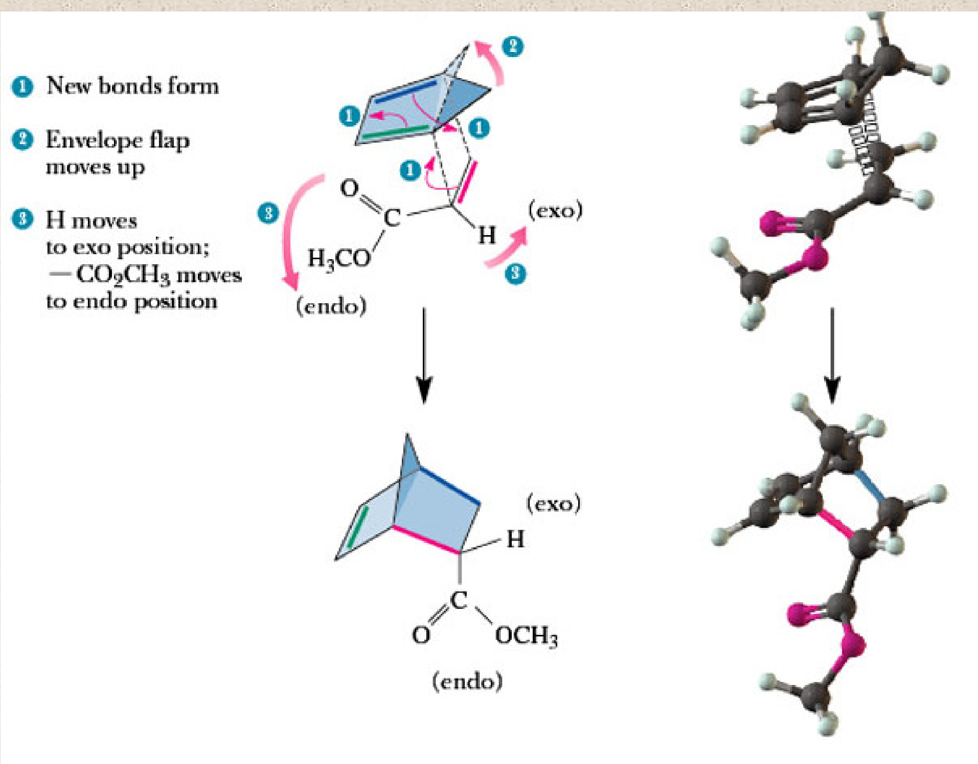


Summary



The carbonyl group on the dienophile is endo (tucked inside)

Summary



① New bonds form

② Envelope flap moves up

③ H moves to exo position; $-CO_2CH_3$ moves to endo position