

Reações Pericíclicas

1. Reações Eletrocíclicas

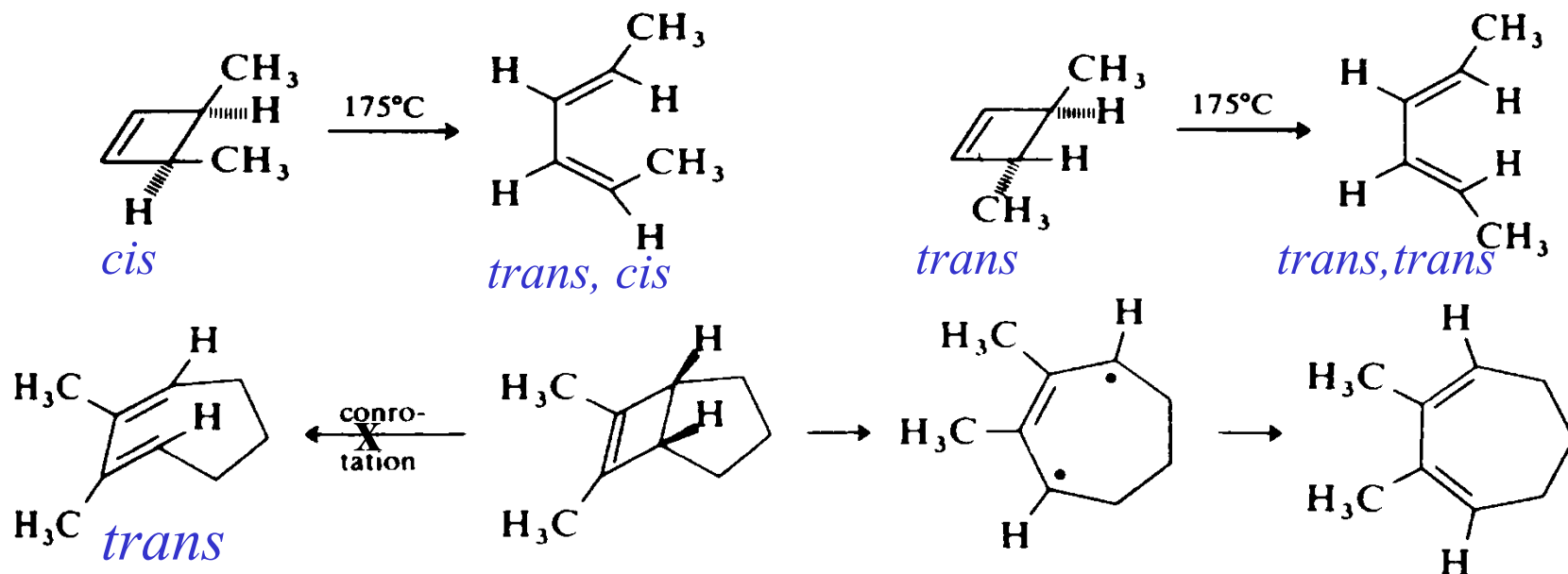
1.1. Teoria de orbitais de fronteira

1.2. Diagramas de correlação de orbitais

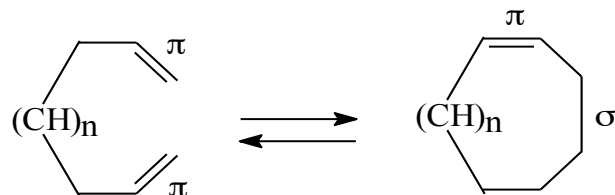
1.3. Estado de transição aromático / antiaromático

2. Rearranjos Sigmatrópicos

3. Reações de Ciclo-adições



1. Reações Eletrocíclicas



1.1. Teoria dos Orbitais de Fronteira

- escolher o orbital de fronteira: HOMO (Δ / S_0) ou LUMO ($h\nu / S_1$)
- fazer a interação de orbitais: conrotatório (CON) disrotatório (DIS)
- interação ligante (permitido) ou antiligante (proibido)

Butadieno / Ciclobuteno: CON vs. DIS:

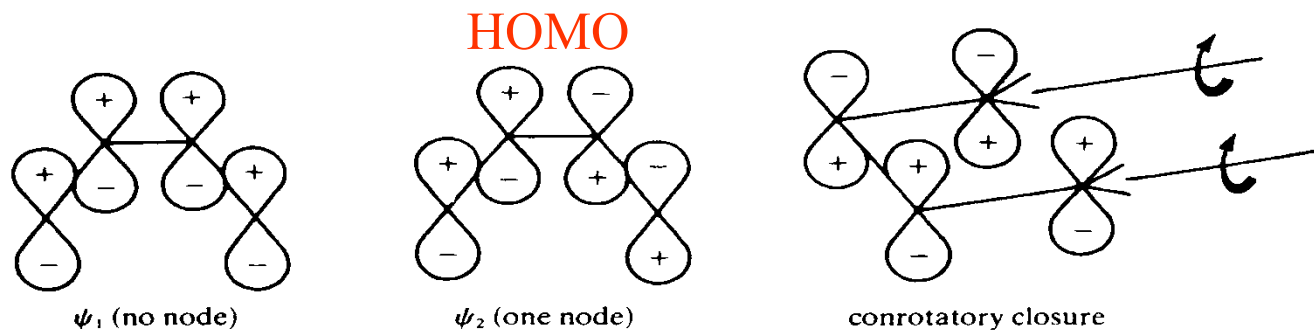


Fig. 11.1. Symmetry properties for the π system of a conjugated diene.

Hexatrieno / Ciclo-hexadieno: CON vs. DIS

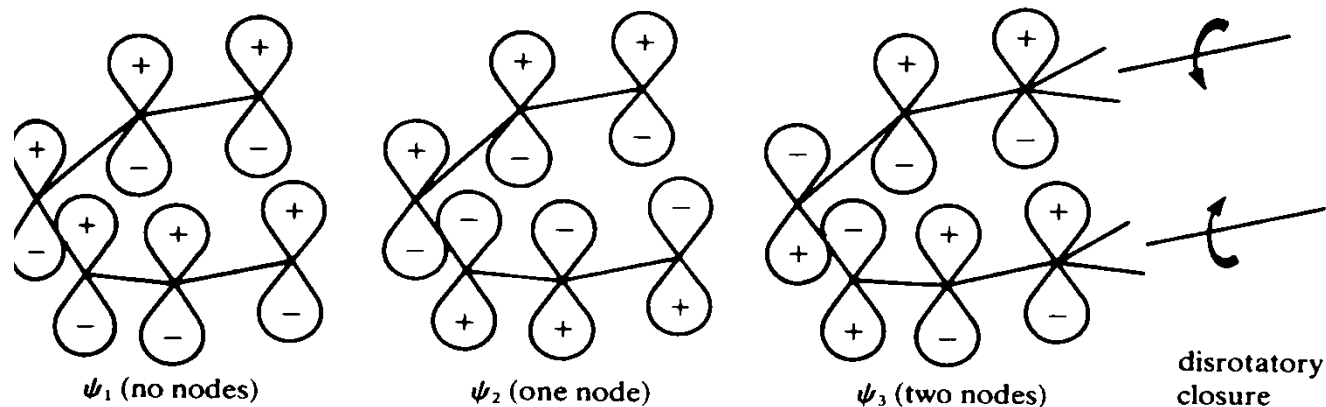
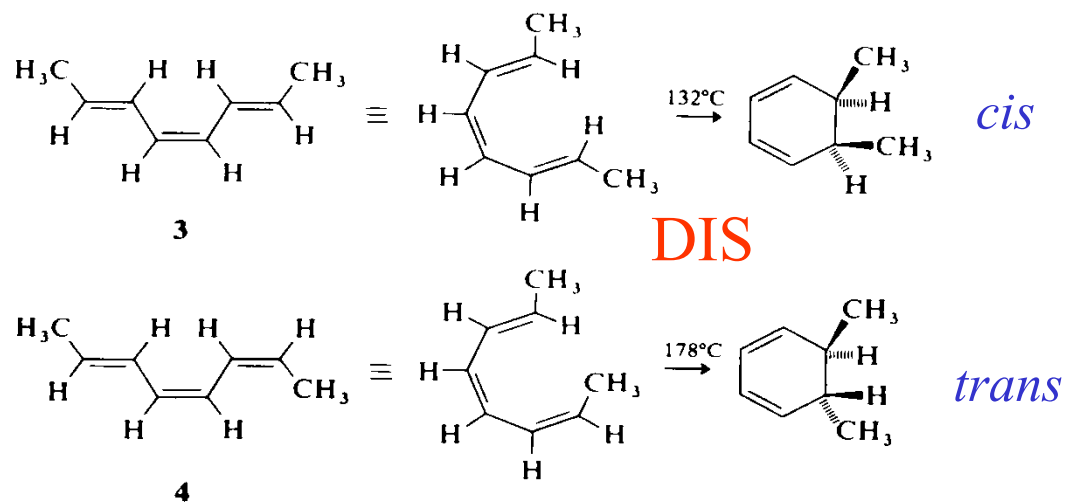


Fig. 11.2. Symmetry properties of hexatriene molecular orbitals.

Exemplos:

Estereoquímica



1.2. Diagramas de Correlação de Orbitais

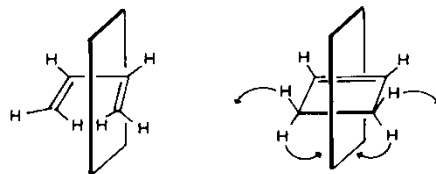
orbitais moleculares do(s) reagente(s) e do(s) produto(s)

classificação pelos elementos de simetria

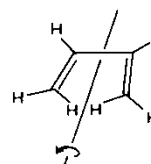
DIS: plano (σ)

CON: eixo (C_2)

Elementos de simetria:



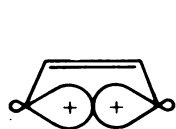
disrotatory plane of symmetry



conrotatory axis of symmetry

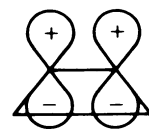
σ

classification with respect to the plane:



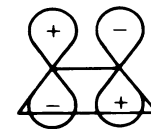
σ

S



π

S



π^*

A



σ^*

A

C_2

classification with respect to the axis:

S

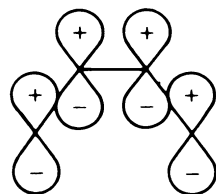
A

S

A

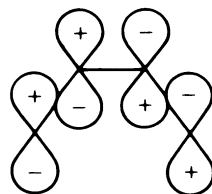
σ

classification with respect to the plane:



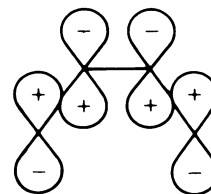
ψ_1

S



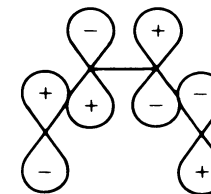
ψ_2

A



ψ_3

S



ψ_4

A

C_2

classification with respect to the axis:

A

S

A

S

Fig. 11.3. Symmetry properties of cyclobutene and butadiene orbitals.

Construção dos Diagramas

- colocar os orbitais conforme a energia
- conectar orbitais da mesma simetria e próximos em energia
- verificar a correlação entre orbitais ligantes / antiligantes

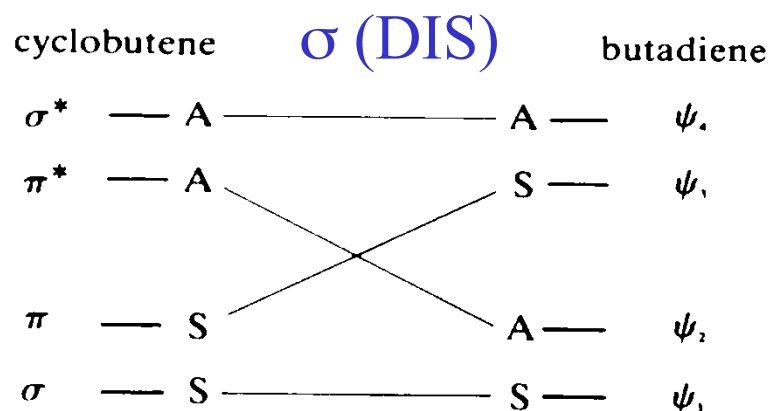


Fig. 11.4. Correlation diagram for cyclobutene and butadiene orbitals (symmetry-forbidden disrotatory reaction).

PROIBIDO

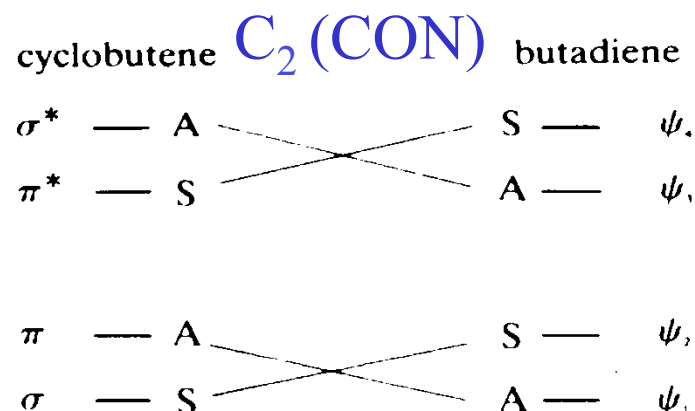


Fig. 11.5. Correlation diagram for cyclobutene and butadiene orbitals (symmetry-allowed conrotatory reaction).

PERMITIDO

1.3. Teoria do Estado de Transição Aromático vs. Anti-Aromático

butadieno - ciclobuteno



basis set orbitals
for conrotatory closure

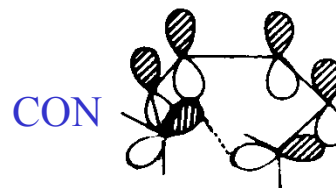
1 nó: Möbius
4n elétrons
permitida



basis set orbitals
for disrotatory closure

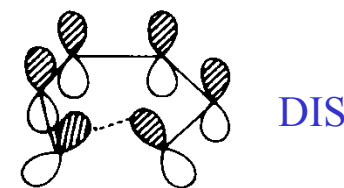
0 nó: Hückel
4n elétrons
proibida

hexatrieno - ciclo-hexadieno



conrotatory:
Möbius system

1 nó: Möbius
4n+2 elétrons
proibida



disrotatory:
Hückel system

0 nó: Hückel
4n+2 elétrons
permitida

Sistemas permitidos:

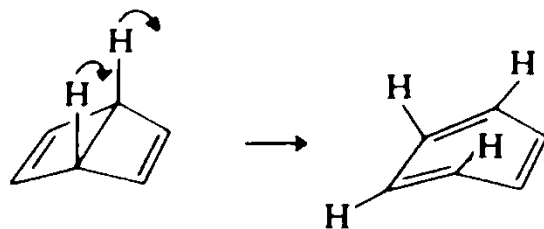
Hückel (0 ou n° par de nós) com (4π+2) elétrons

Möbius (N° impar de nós) com (4π) elétrons

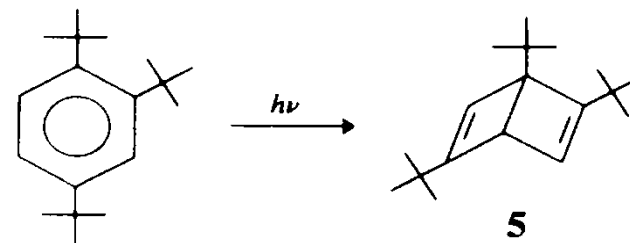
| Electrons | Hückel (disrotatory) | Möbius (conrotatory) |
|-----------|-------------------------|-------------------------|
| 2 | aromatic | antiaromatic |
| 4 | antiaromatic | aromatic |
| 6 | aromatic | antiaromatic |
| 8 | antiaromatic | aromatic |

EXEMPLOS

Benzeno de Dewar:

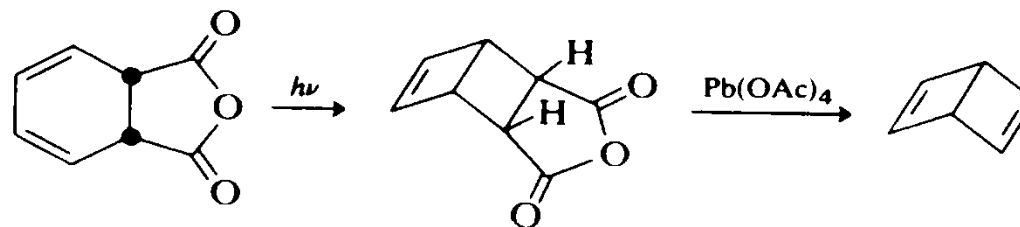


4n elétrons: CON; C=C *trans*
processo DIS: est. excitado



Tamelen, Pappas & Kirk (1962)

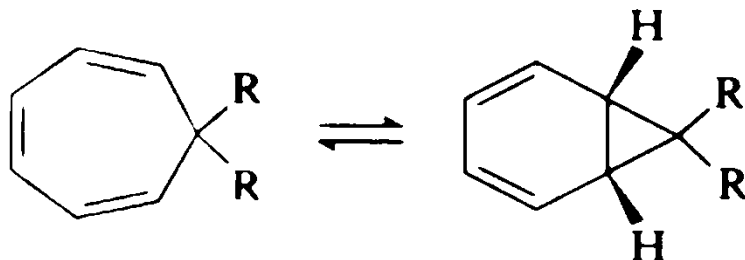
Preparação do benzeno de Dewar: Tamelen, Pappas & Kirk (1963)



Tempo de meia vida: 2 dias a 25°C;
entalpia de ativação: $\Delta H^\ddagger = 23$ kcal/mol

EXEMPLOS - II

Ciclo-heptatrieno - Norcaradieno (biciclo [4.1.0] hepta-2,4-dieno):



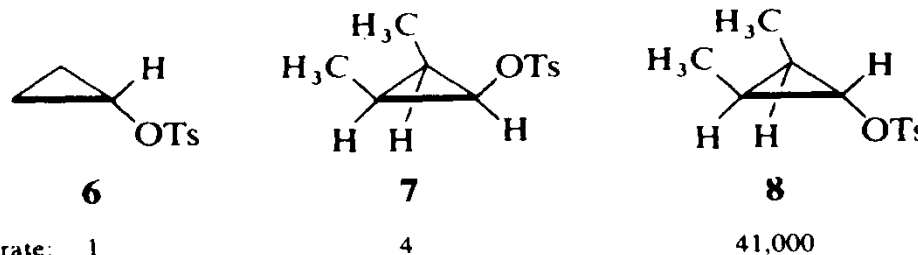
6 elétrons: DIS

equilíbrio rápido; sistema π do anel *s-cis,s-cis*
 $R = CO_2R'$: $\Delta H^\ddagger = 7 \text{ kcal/mol}$ (RMN)

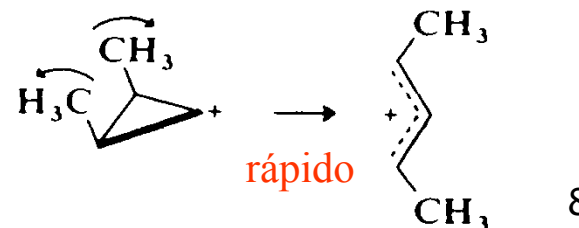
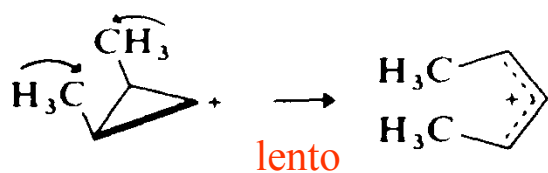
Cátion ciclopropila: 2 elétrons DIS



Envolvimento do cátion “livre”?

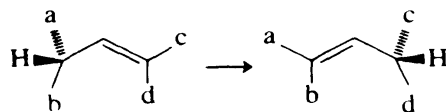


assistência anquimérica: processo concertado

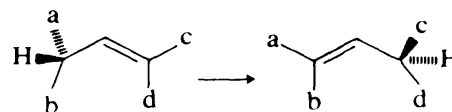


2. Rearranjos Sigmatrópicos

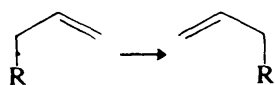
Exemplos de Rearranjos Sigmatrópicos



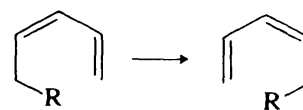
1,3-suprafacial shift of hydrogen



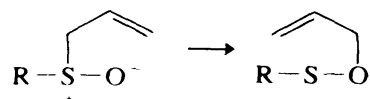
1,3-antarafacial shift of hydrogen



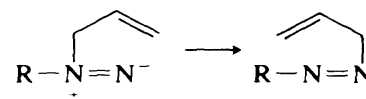
1,3-shift of alkyl group



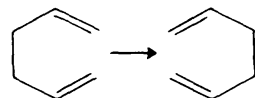
1,5-shift of alkyl group



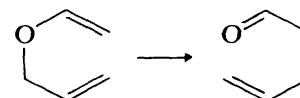
2,3-sigmatropic rearrangement of an allyl sulfoxide



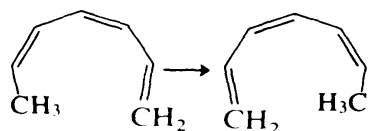
2,3-sigmatropic rearrangement of an allyl diazene



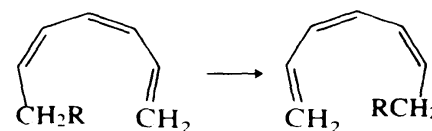
3,3-sigmatropic rearrangement of a 1,5-hexadiene



3,3-sigmatropic rearrangement of an allyl vinyl ether



1,7-sigmatropic shift of hydrogen



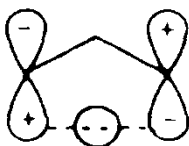
1,7-sigmatropic shift of an alkyl group

Deslocamento de Hidrogênio

Teoria de Orbitais de Fronteira:

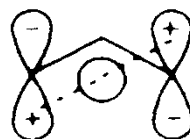
Deslocamento 1,3 de H:

proibido



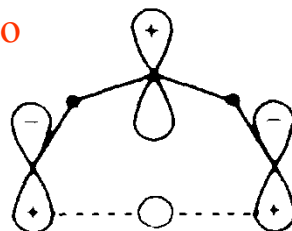
suprafacial

permitido porém: geometria!!



antarafacial

Desloc. 1,5 de H: permitido



thermally allowed 1,5-suprafacial hydrogen shift in 1,3-pentadiene

Deslocamento de Hidrogênio e Carbono

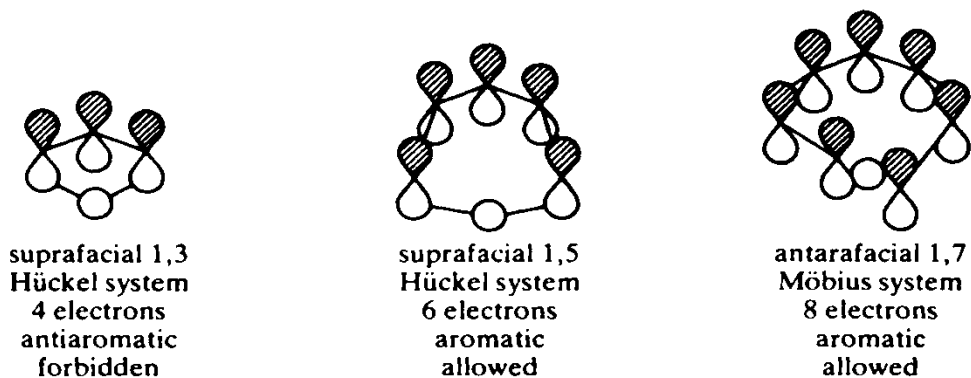


Fig. 11.6. Classification of sigmatropic hydrogen shifts with respect to basis set orbitals.

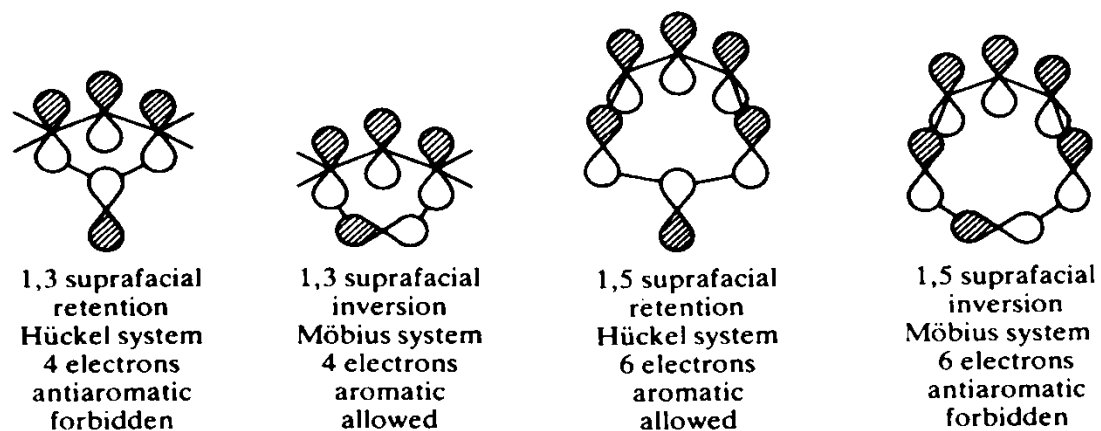


Fig. 11.7. Classification of sigmatropic shifts of alkyl groups with respect to basis set orbitals.

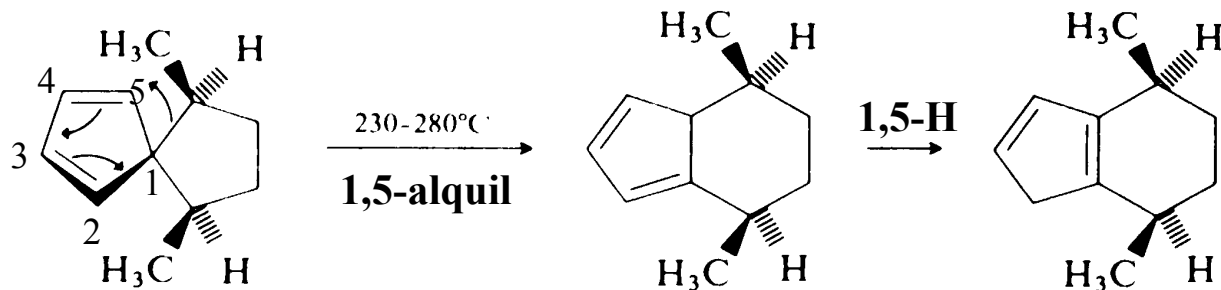
Regras Gerais de Seleção

Scheme 11.2. Generalized Selection Rules for Sigmatropic Processes

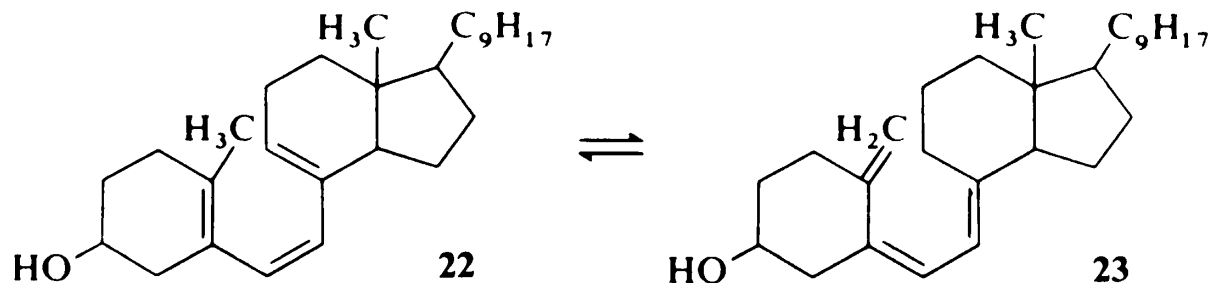
| Selection rules for sigmatropic shifts of order $[i, j]$ | | | | |
|--|-----------------|-----------------|------------------|------------------|
| A. Order $[1, j]$ | | | | |
| $1 + j$ | supra/retention | supra/inversion | antara/retention | antara/inversion |
| $4n$ | forbidden | allowed | allowed | forbidden |
| $4n + 2$ | allowed | forbidden | forbidden | allowed |
| B. Order $[i, j]$ | | | | |
| $i + j$ | supra/supra | supra/antara | antara/antara | |
| $4n$ | forbidden | allowed | forbidden | |
| $4n + 2$ | allowed | forbidden | allowed | |

Exemplos de Rearranjos Sigmatrópicos

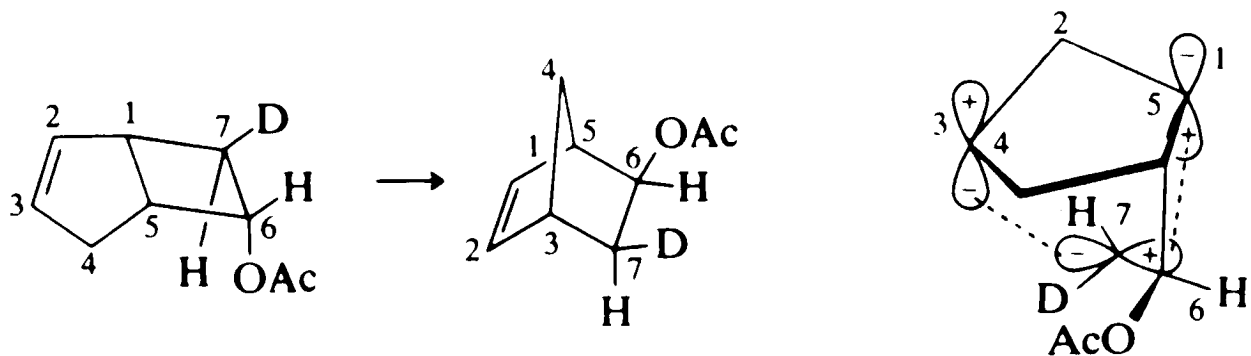
1,5-alquil: 6π ,
supra-retenção



1,7-H: 8π ,
antara-(retenção)

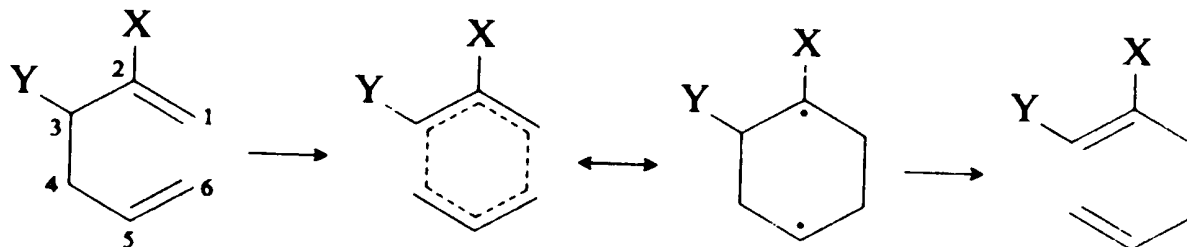


1,3-alquil: 4π ,
supra-inversão

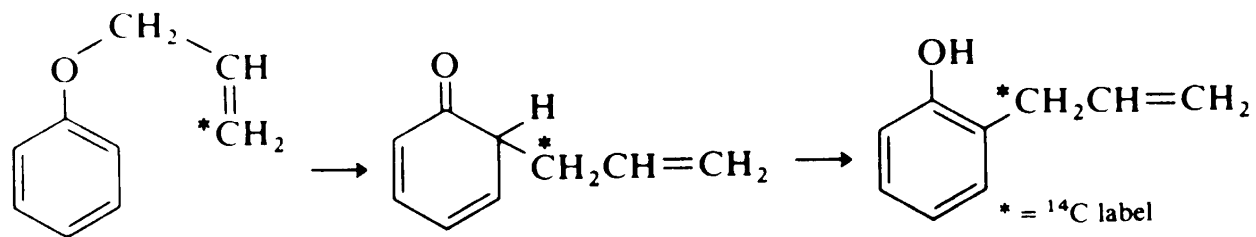


Rearranjos de Cope e Claisen [3,3]

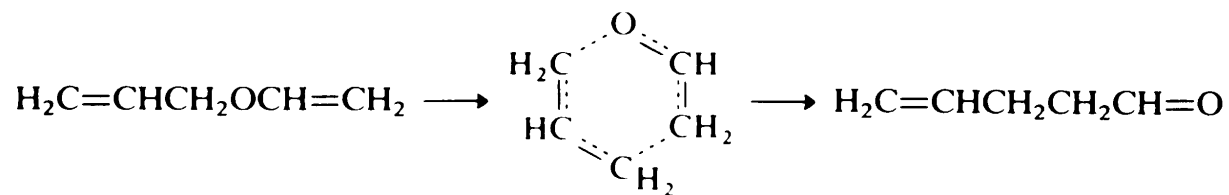
Rearranjo de Cope (esquema geral):



Rearranjo de Claisen (aromático):

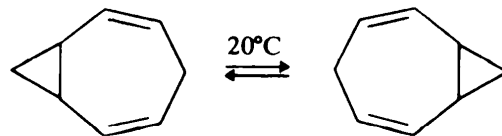


Rearranjo de Claisen (alifático):



Exemplos de Rearranjos de Cope

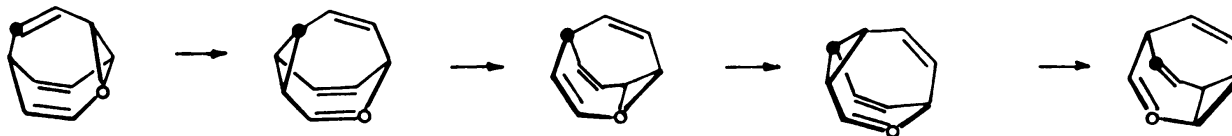
Homotropilideno



homotropilidene
36

T baixa: 4 H vinílicos, 2 H alílicos
4 H ciclopropílicos
T alta: 2 vinílicos inalterados;
2 vinílicos coalecem com ciclopropílicos
2 alílicos coalecem com ciclopropílicos

Bulvaleno



a 25°C: $k_1 = 3440 \text{ s}^{-1}$; a 100 °C: somente 1 pico no RMN, $\delta = 4,22 \text{ ppm}$

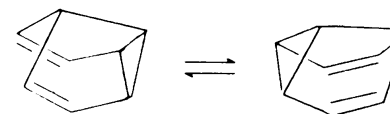
Barbaraleno



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a 25°C: $k_1 = 10^7 \text{ s}^{-1}$; $\Delta G^\ddagger = 7,6 \text{ kcal/mol}$: 4 pico s no RMN

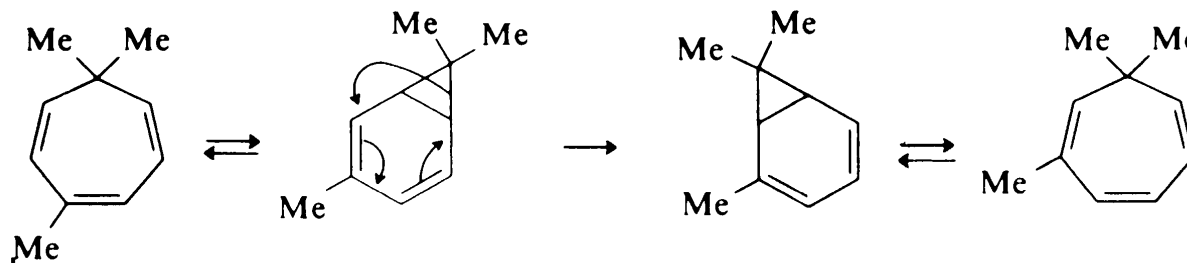
Semibulvaleno



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$\Delta G^\ddagger (-143^\circ\text{C}) = 5,5 \text{ kcal/mol}$;
mais rápido que inversão do ciclo-hexano

Isomerização de Ciclo-Hexatrienos Substituídos:



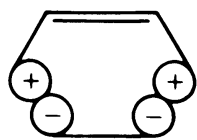
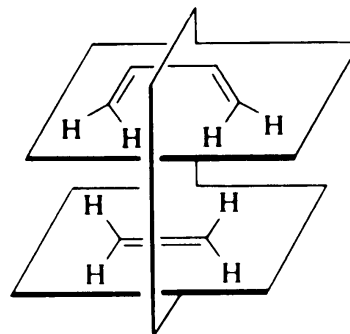
3. Ciclo-adição:

3.1. Ciclo-adição [4+2]: Diagrama de Orbitais

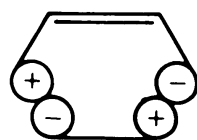
Interação do dieno suprafacial e do etileno suprafacial

[4s + 2s]

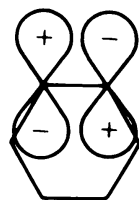
Elemento de simetria: plano σ



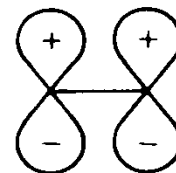
$\sigma_{1(e)}^*$
symmetric (S)



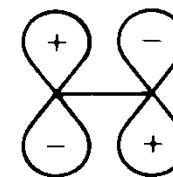
$\sigma_{2(e)}^*$
antisymmetric (A)
cyclohexene orbitals



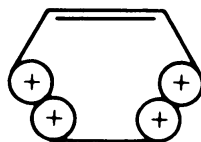
$\pi_{(e)}^*$
antisymmetric (A)



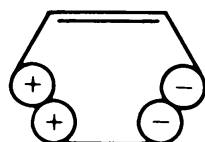
$\psi_{1(e)}$
symmetric (S)



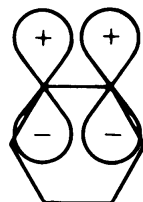
$\psi_{2(e)}$
antisymmetric (A)
ethylene orbitals



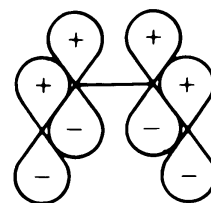
$\sigma_{1(e)}$
symmetric (S)



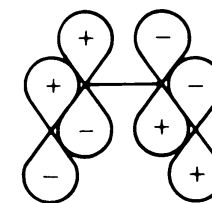
$\sigma_{2(e)}$
antisymmetric (A)



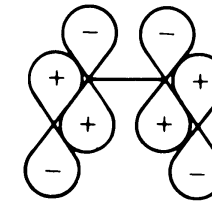
$\pi_{(e)}$
symmetric (S)



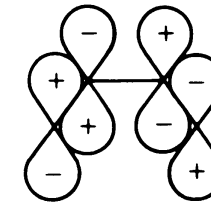
$\psi_{1(b)}$
symmetric (S)



$\psi_{2(b)}$
antisymmetric (A)

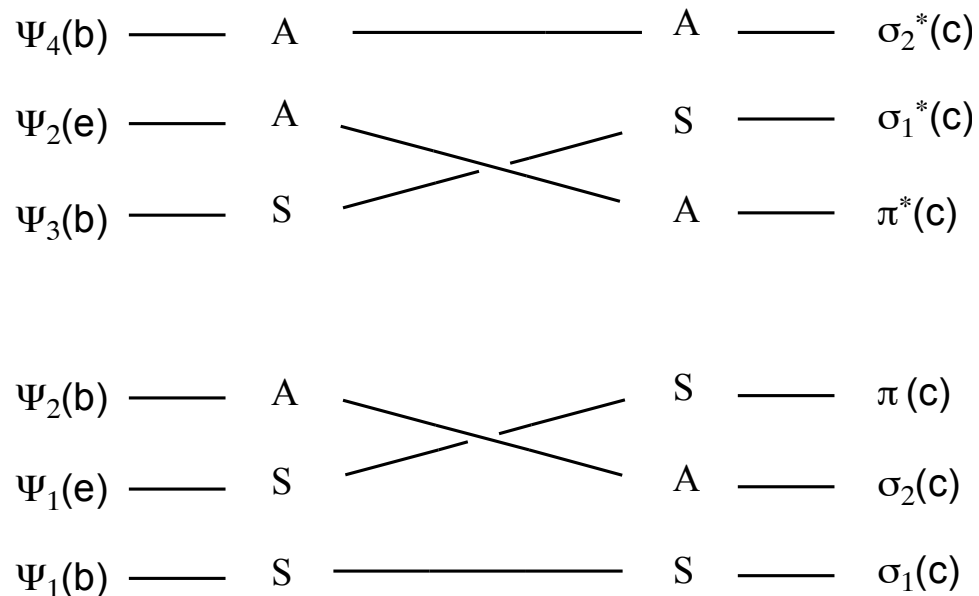


$\psi_{3(b)}$
symmetric (S)



$\psi_{4(b)}$
antisymmetric (A)
butadiene orbitals

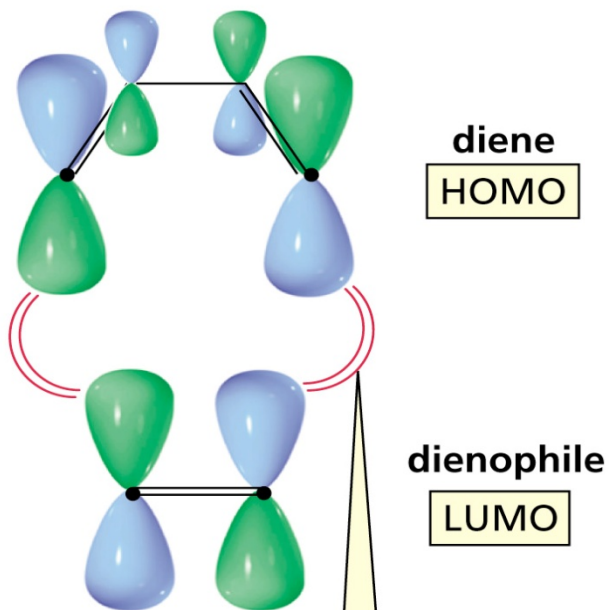
Diagrama de Correlação dos Orbitais: Ciclo-adição [4+2]



Correlação somente **entre orbitais ligante** dos reagentes com orbitais ligantes dos produto: transformação [4s + 2s] **permitida**

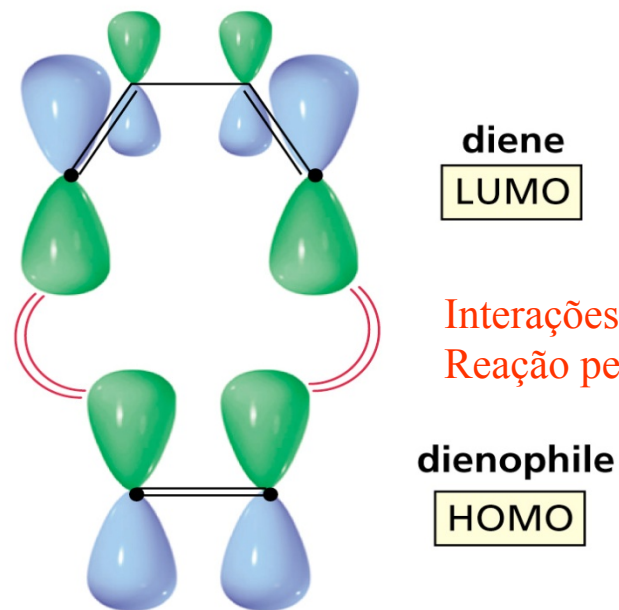
Orbitais de Fronteira: Ciclo-adição [4s + 2s]

a.



Interações ligantes:
Reação permitida

b.



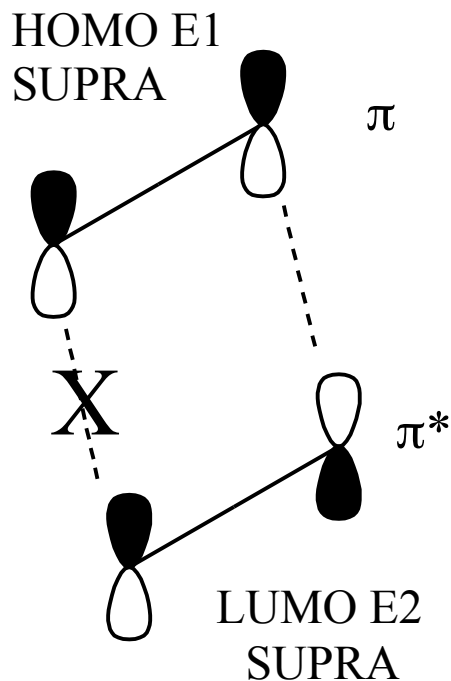
Interações ligantes:
Reação permitida

Sobreposição entre orbitais
da mesma cor / fase: **LIGANTE**

Orbitais de Fronteira: Cicloadição [2 + 2]

Supra - Supra:

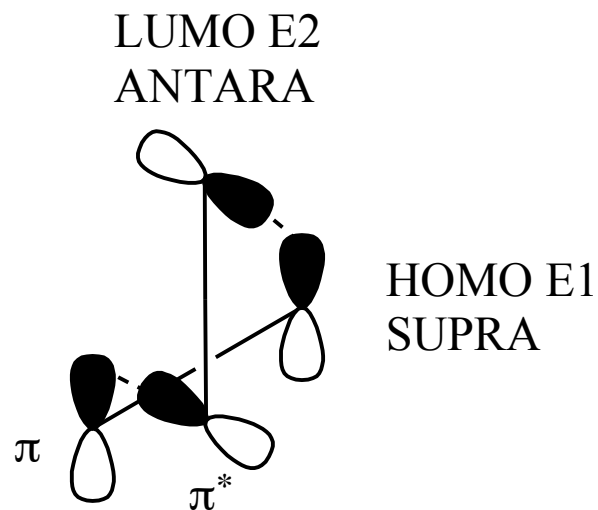
HOMO (π) etileno 1 e
LUMO (π^*) etileno 2



Uma interação anti-ligante:
Supra - Supra proíbia

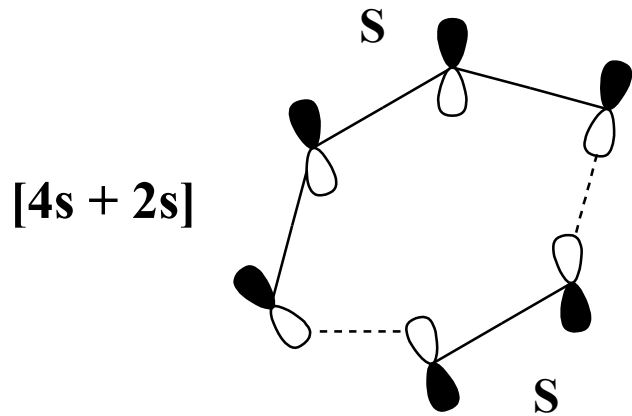
Supra - Antara:

HOMO (π) etileno 1 e
LUMO (π^*) etileno 2

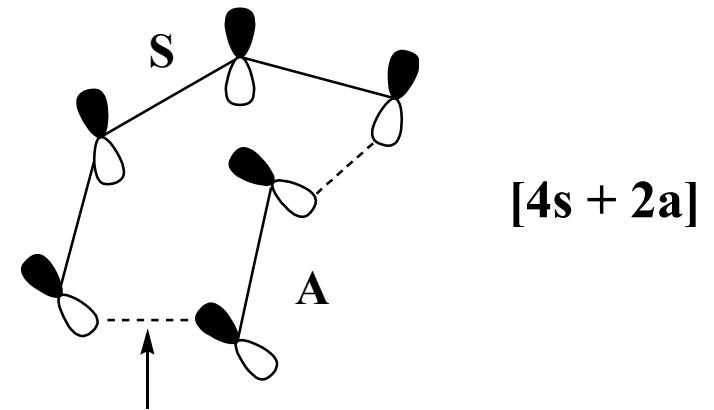


Só interações ligantes:
Supra - Antara permitida

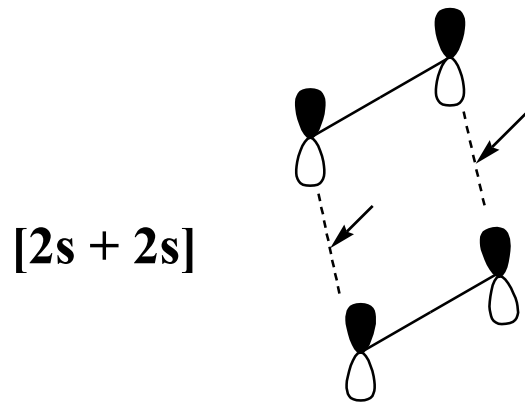
Estado de Transição Aromático – Anti-aromático



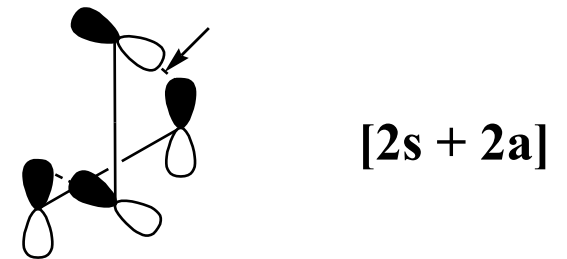
0 nós / Hückel / 6 e⁻
Aromático / **permitido**



1 nós / Möbius / 6 e⁻
Anti-aromático / **proibido**

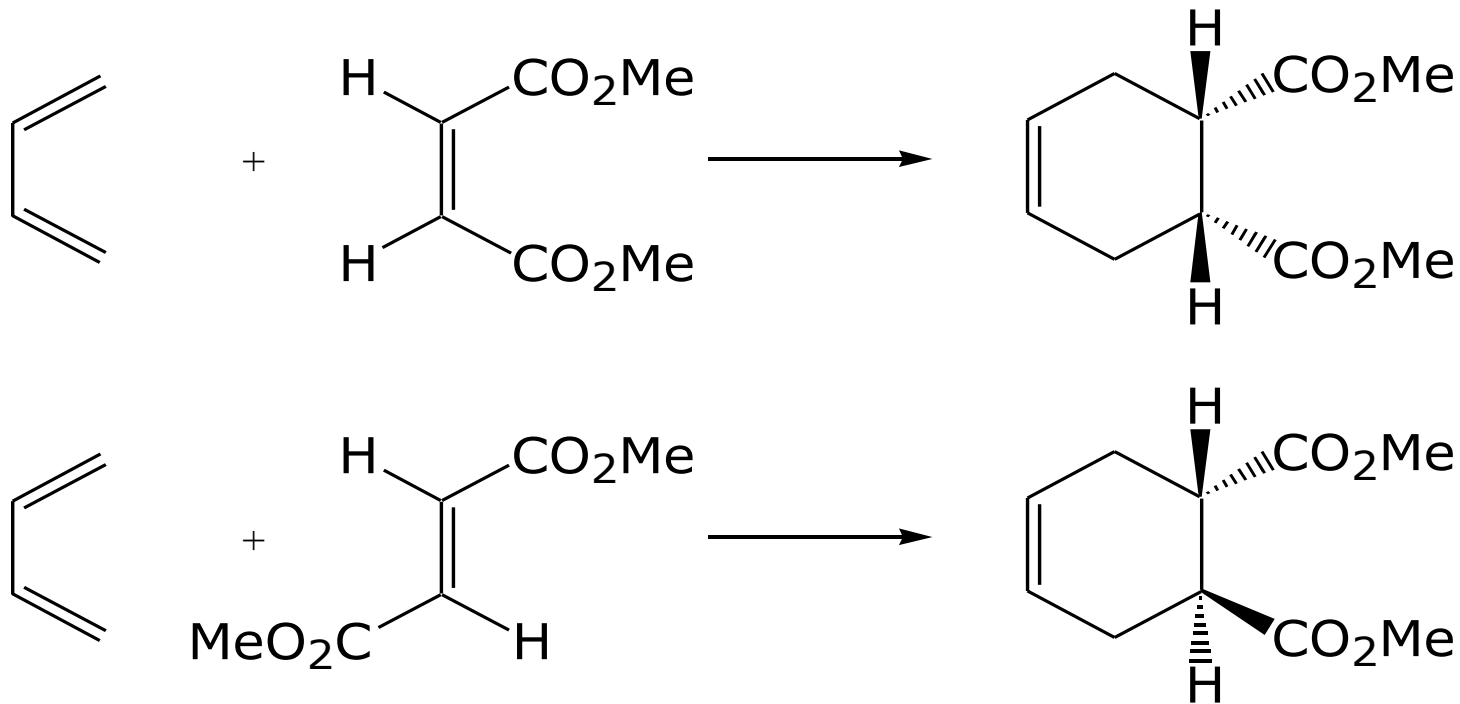


2 nós / Hückel / 4 e⁻
Anti-aromático / **proibido**



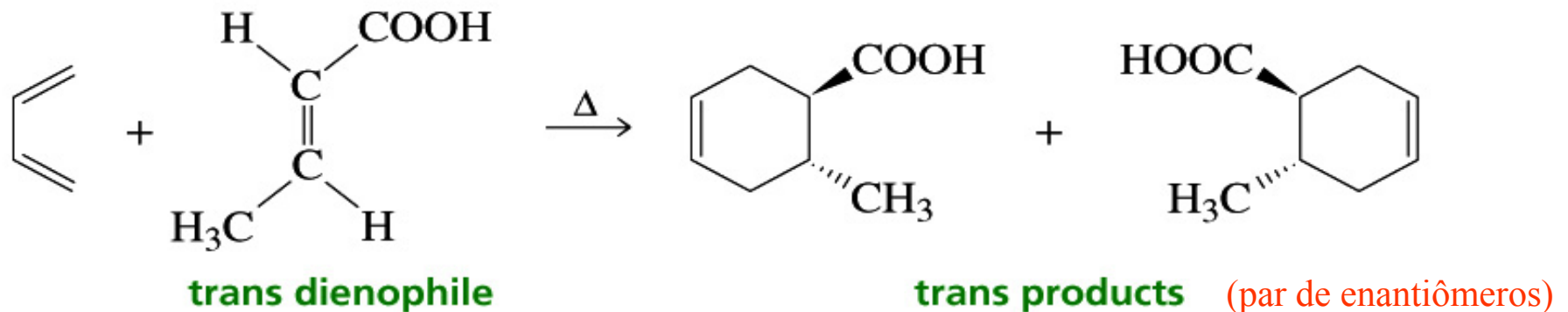
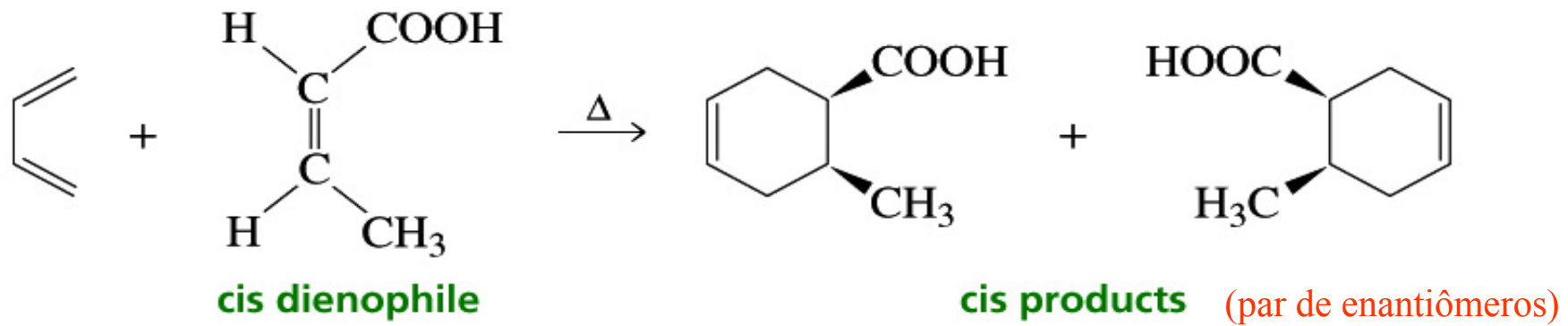
1 nós / Möbius / 4 e⁻
Aromático / **permitido**

Estereoquímica da Reação de Diels-Alder:



a configuração do **dienófilo** é mantida no produto final; adição **SIN**

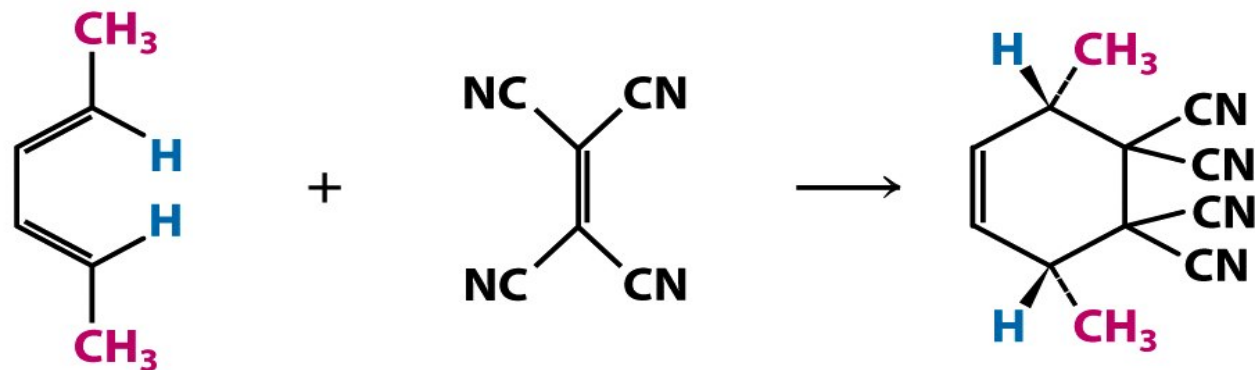
Estereoquímica da Reação de Diels-Alder:



- A reação Diels–Alder é **estereoespecífica**.
- A configuração dos reagentes (tanto dienófilo quanto dieno) é **mantida**.
- Trata-se de uma reação **concertada**.

Estereoquímica da Reação de Diels-Alder:

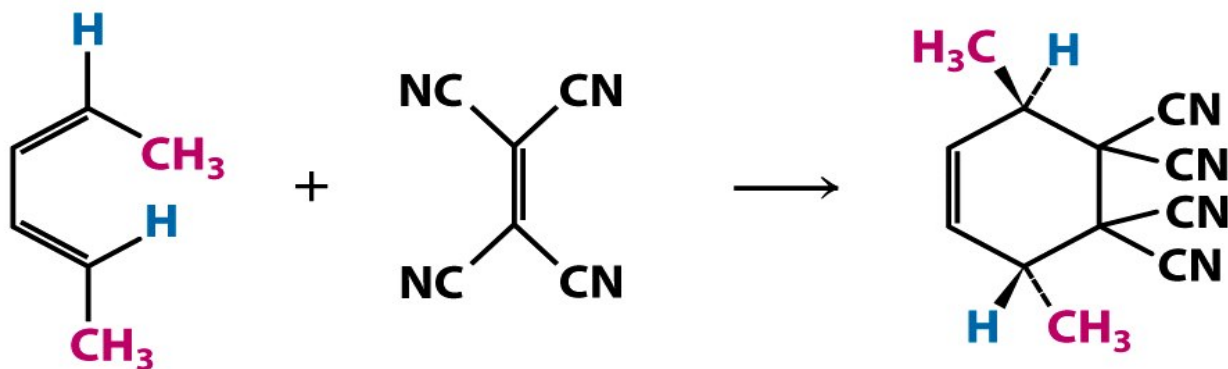
a configuração do **dieno** é mantida no produto final; adição **SIN**



trans,trans-2,4-hexadieno

tetraciano-etileno

grupos metila em *cis*

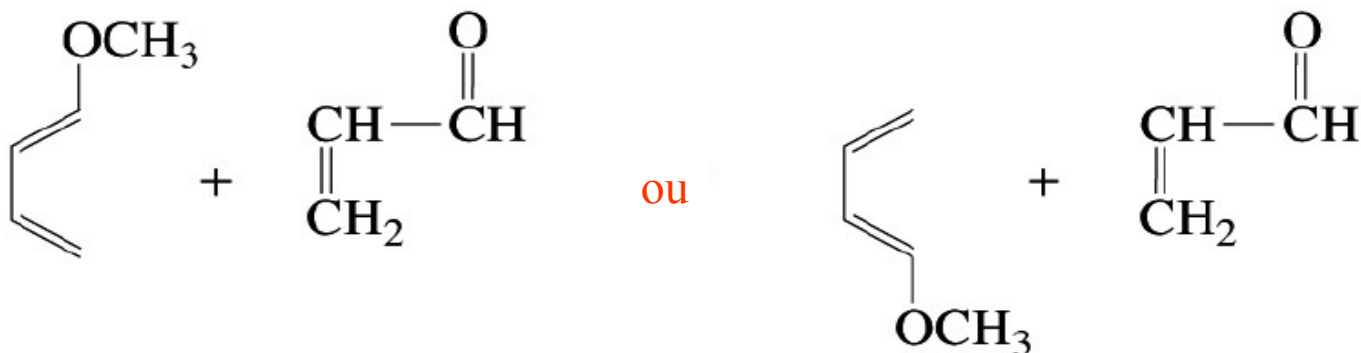


cis,trans-2,4-Hexadieno

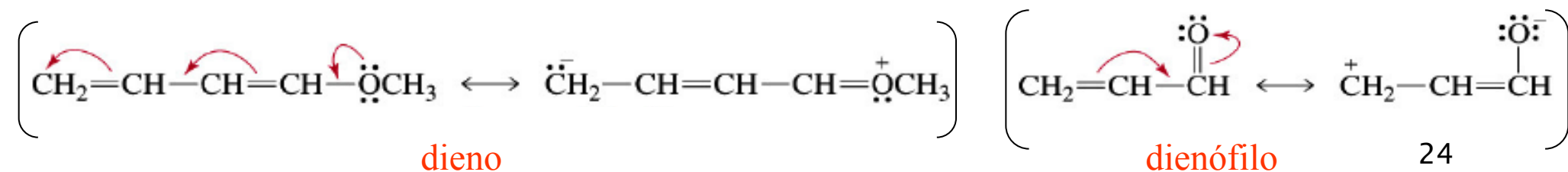
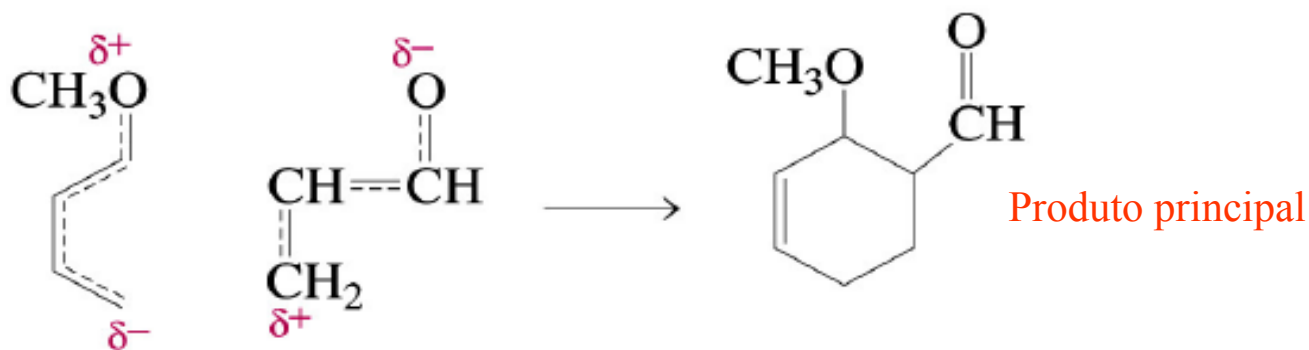
grupos metila em *trans*

Predição dos Produtos com Reagentes não Simétricos

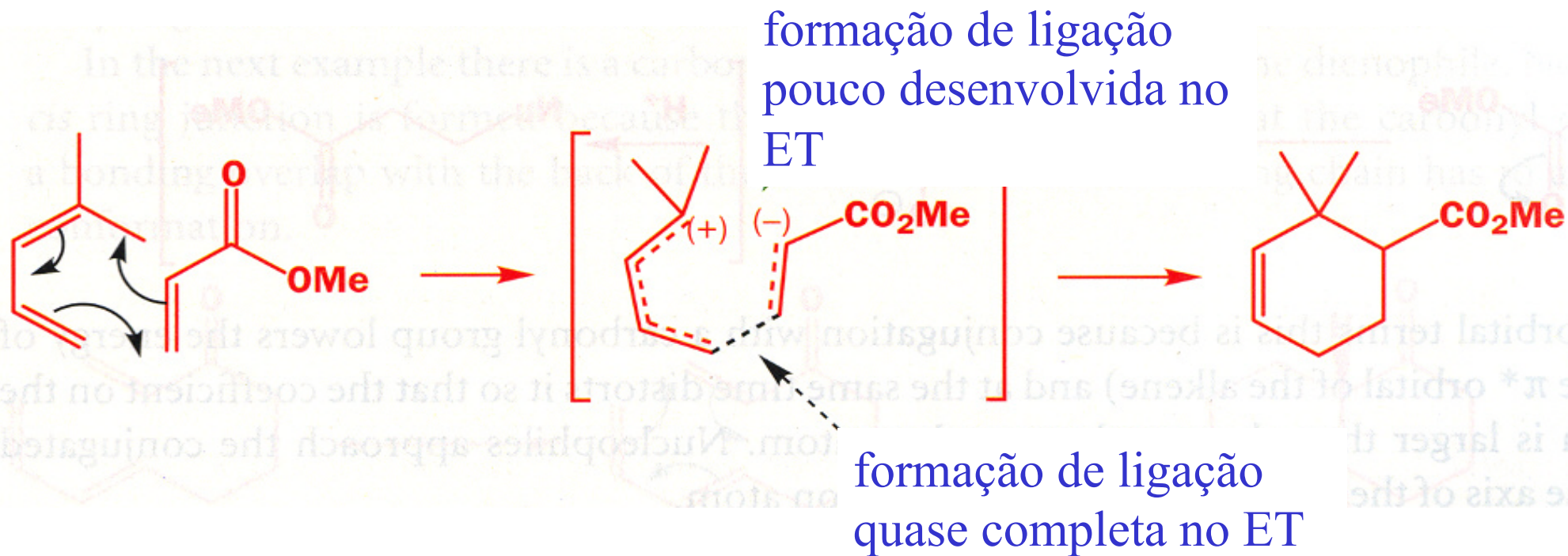
1. Possibilidades de Reação



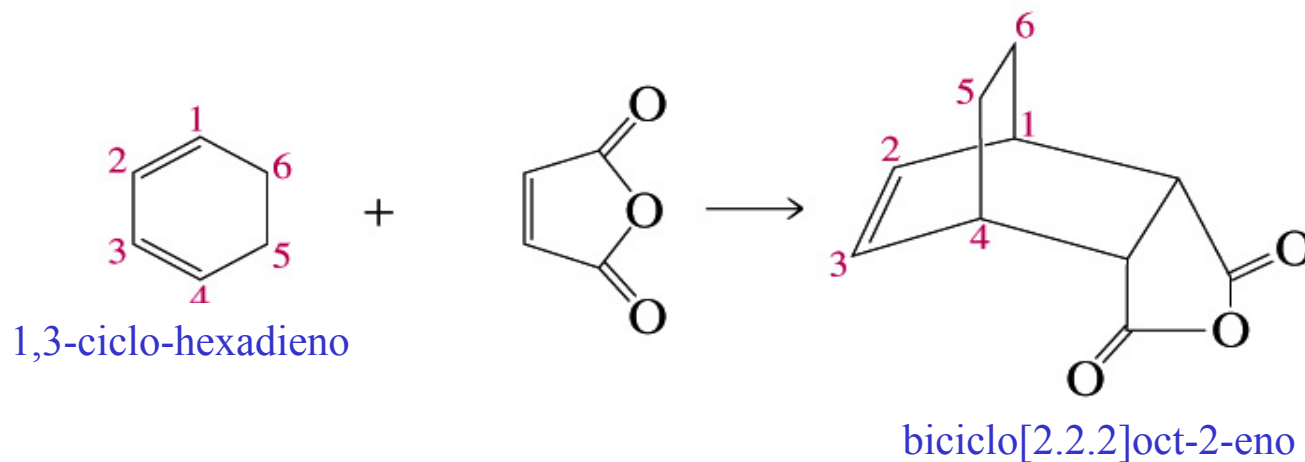
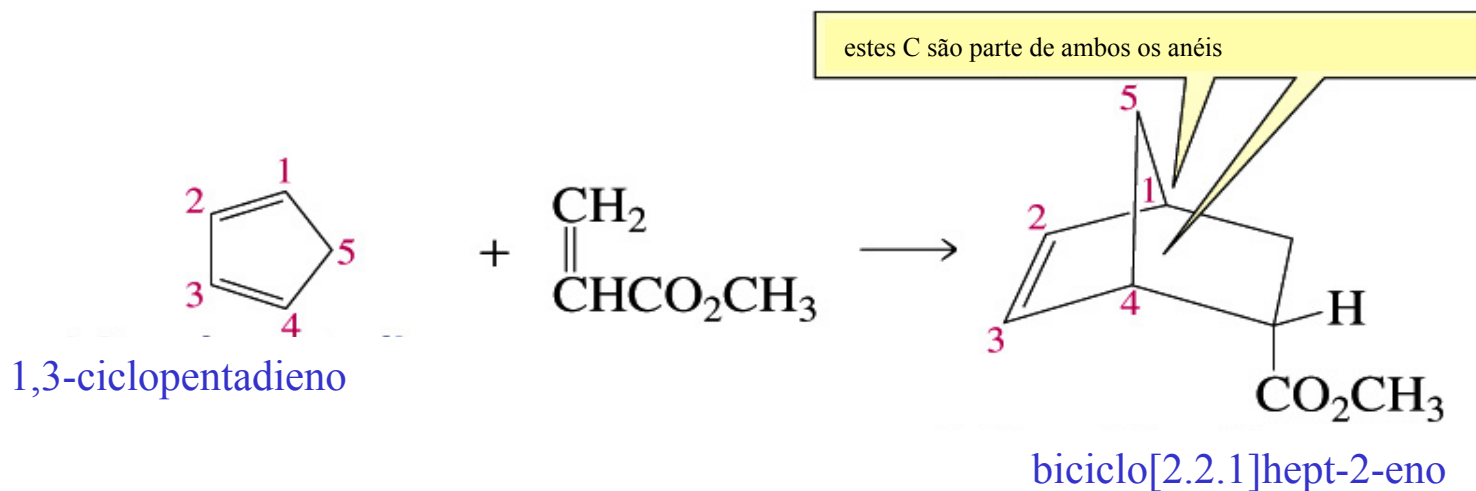
2. Considerando-se a Distribuição de Cargas nas Estruturas de Ressonância



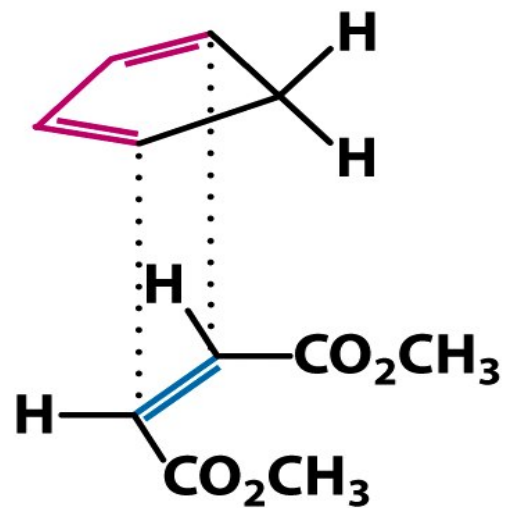
Outro Exemplo de Reação Diels-Alder *Regiosseletiva*.



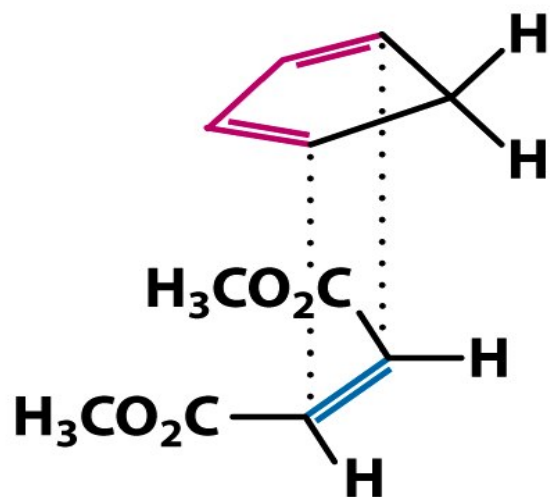
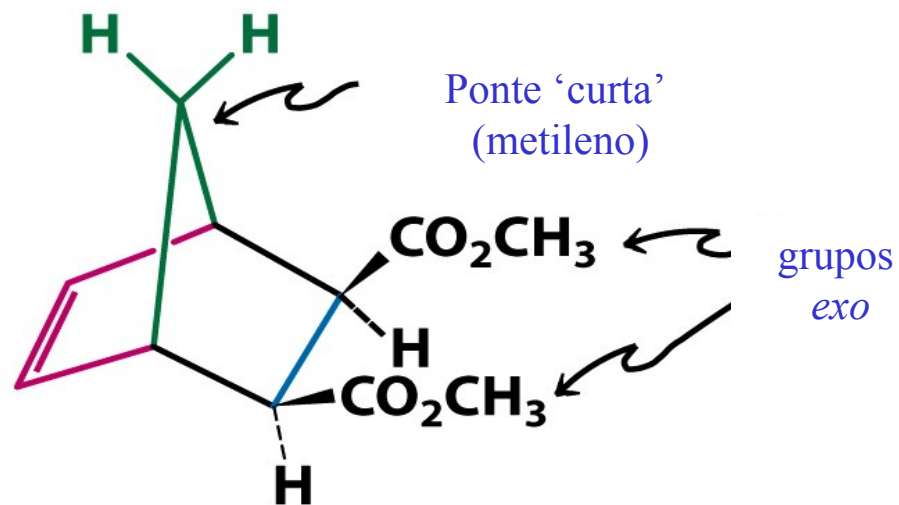
Reação de Dienos Cíclicos: **s-CIS**



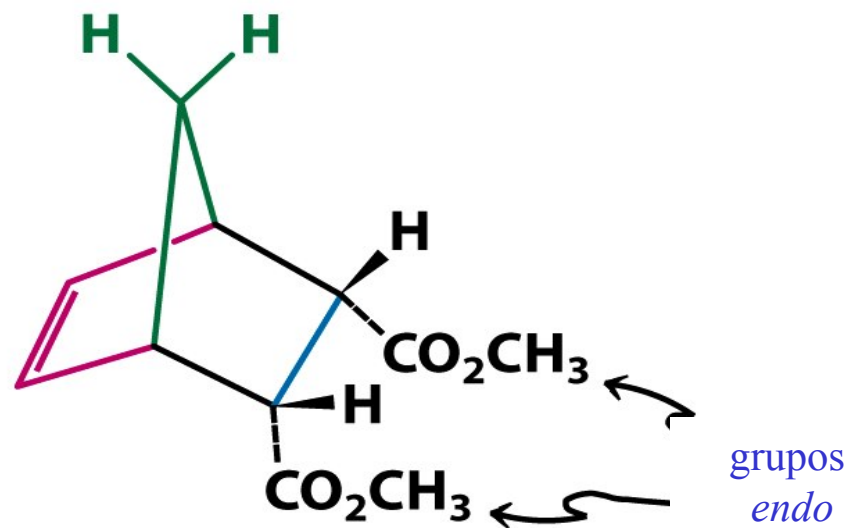
Formação de Produtos *ENDO* e *EXO*



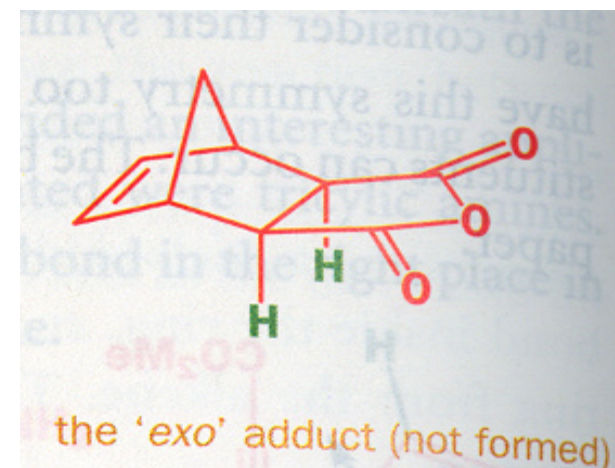
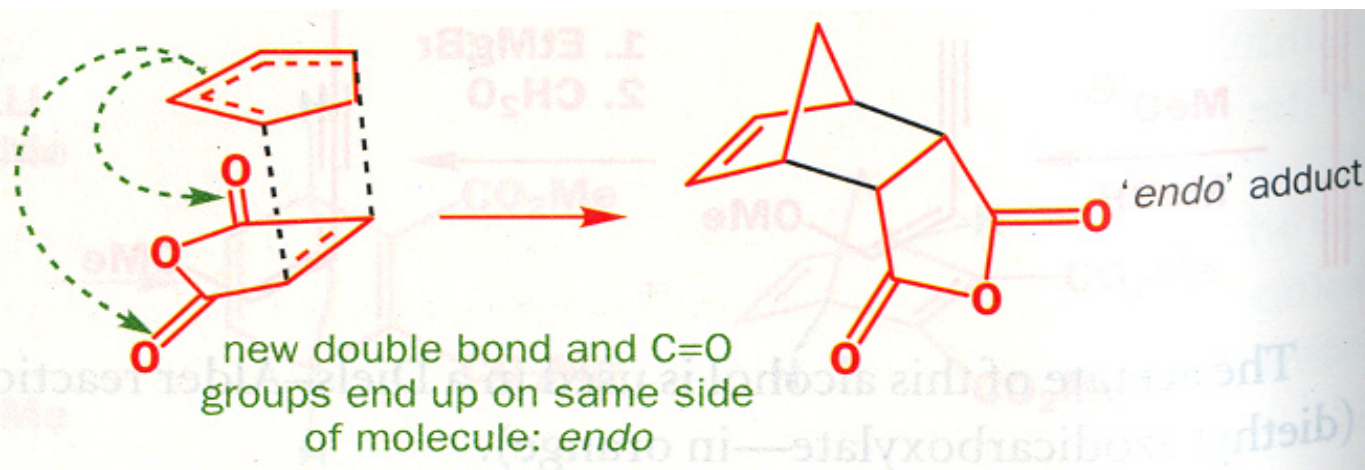
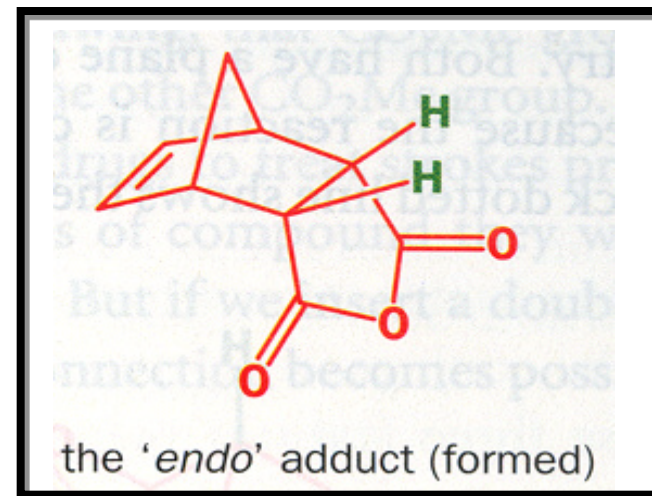
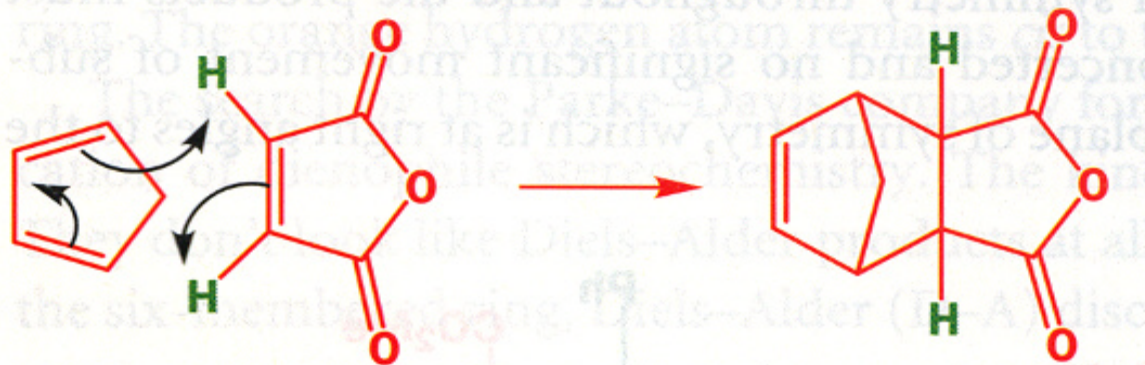
adição *exo*



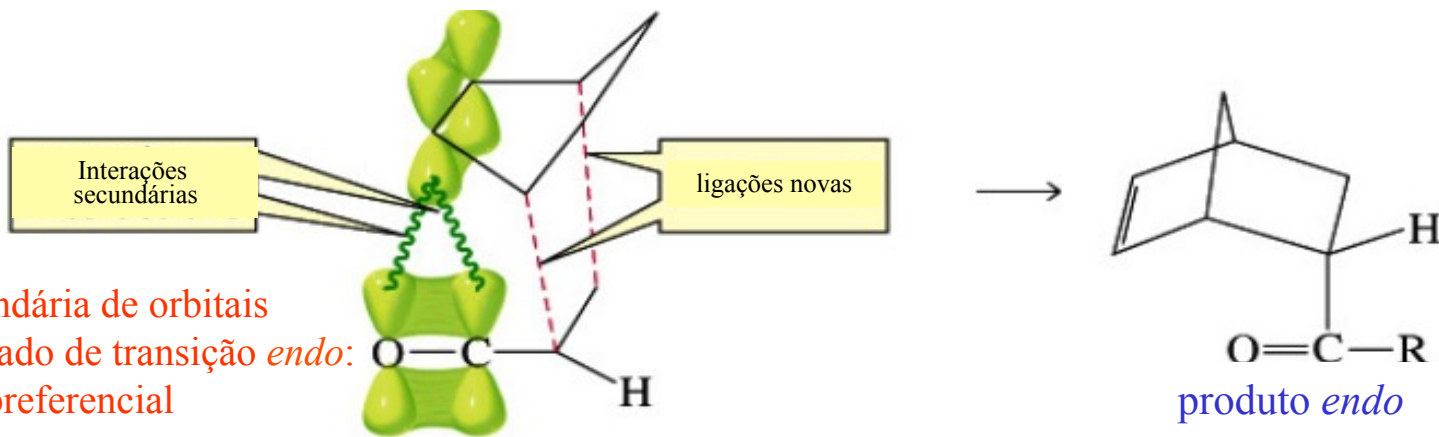
adição *endo*



Formação Preferencial do Produto ENDO: Regra de Alder



Formação do Produto ENDO: Interação Secundária de Orbitais no Estado de Transição



Não há interação secundária de orbitais: produto *exo* formado em menor quantidade

