



CHAPTER 17

PERICYCLIC REACTION

17.1 PERICYCLIC REACTION

17.1.1 Pericyclic Reaction

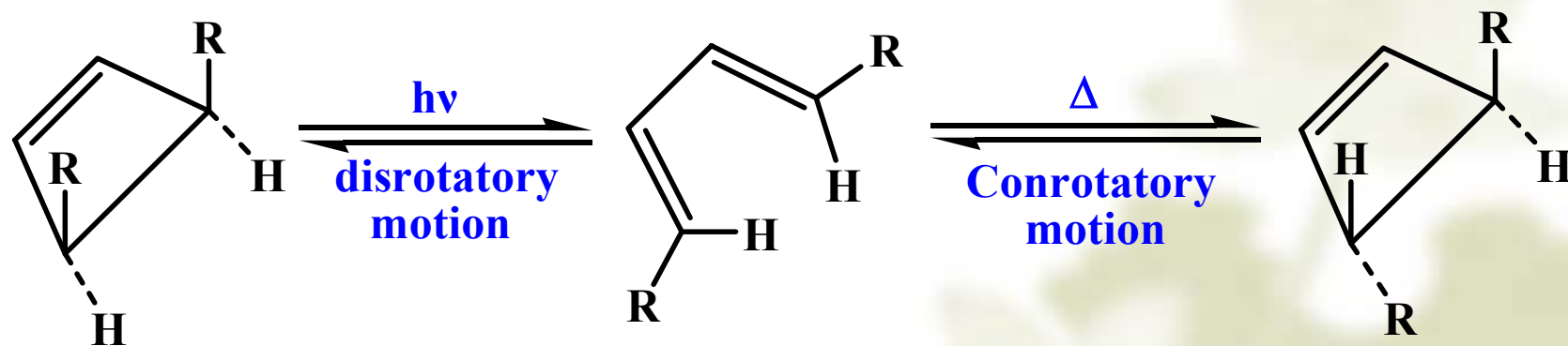
反应特征可以归纳为：

- (1) 反应进行的条件是加热或光照；
- (2) 反应进行时有两个以上的键同时断裂或形成，即多中心一步反应；
- (3) 反应时作用物的变化有突出的立体选择性；
- (4) 在反应过渡态中原子排列是高度有序的。

反应不形成离子或自由基的中间体，不受溶剂极性的影响，不被酸或碱所催化，没有发现任何引发剂对反应有什么作用。

有机化学家认为：这是由电子重新组织经过多中心环状过渡态而进行的一类反应。化学键断裂或生成是同时发生的。这种一步完成的多中心反应叫周环反应（pericyclic reaction）。

Example:



17.1.2 Molecular Orbitals and Chemical Bonds

In 1965, Woodward and Hoffmann formulated their theoretical insights into a set of rules and for **concerted reactions** (协同反应) only.

Definition:

Concerted reactions are reactions in which bonds are **broken and formed simultaneously** and , thus, no intermediates occur.

The Woodward-Hoffmann rules are based on this hypothesis: **In concerted reactions molecular orbitals of the reactant are continuously converted into molecular orbitals of the product.**

轨道对称守恒
原理

According to Woodward-Hoffmann, certain reaction paths are said to be *symmetry allowed*, whereas others are said to be *symmetry forbidden*.

17.1.3 The Frontier Orbital Theory

福井谦一 (K. Fukui) 指出：分子轨道中能量最高的已占轨道 (**HOMO**) 上的电子被束缚得最松弛，最容易被激发到能量最低的空轨道 (**LUMO**) 中去。所以**HOMO**和**LUMO**在周环反应中**至关重要**。

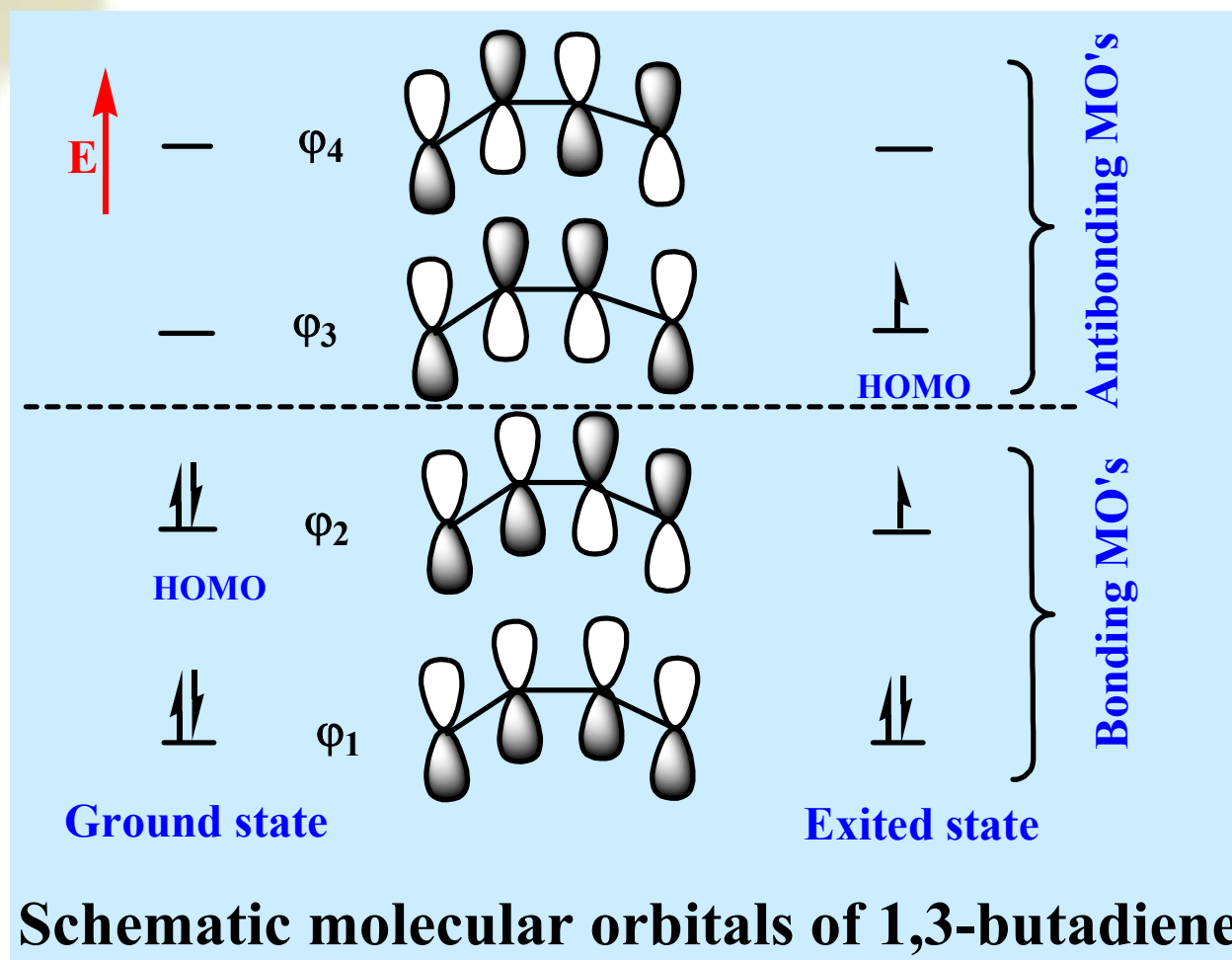
因为这些轨道处于前线，化学键的生成主要在**HOMO**和**LUMO**之间进行，所谓同处前线统称

FMO，所以称为**前线轨道理论 (FMO)**

HOMO: the **highest occupied molecular orbital**

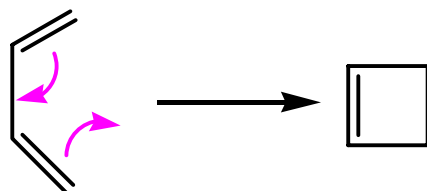
LUMO: the **lowest unoccupied molecular orbital**

Ex: 丁二烯分子4个 π 电子4个 π 轨道。基态时 ψ_2 为HOMO， ψ_3 为LUMO。激发态时 ψ_3 为HOMO， ψ_4 则为LUMO。

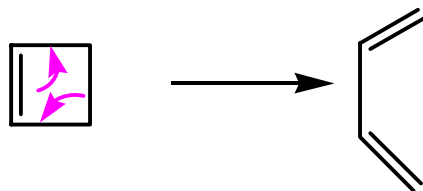


17.2 ELECTROCYCLIC REACTIONS

Definition: A number of reactions, like the one shown here, transform a conjugated polyene into a cyclic compound.



In many other reactions, the ring of a cyclic compound opens and a conjugated polyene forms.

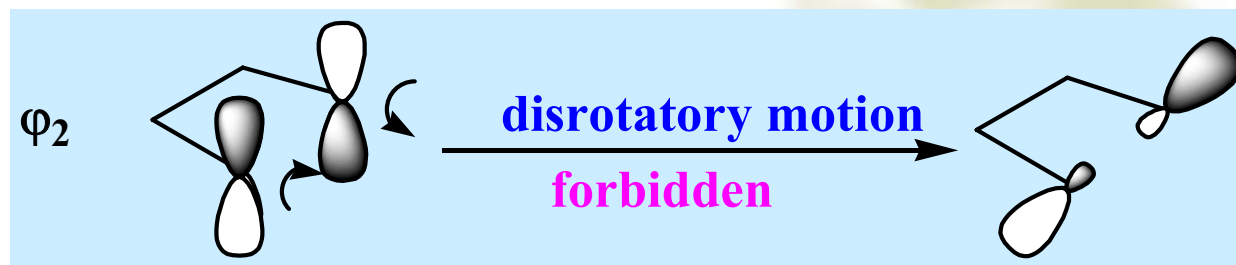
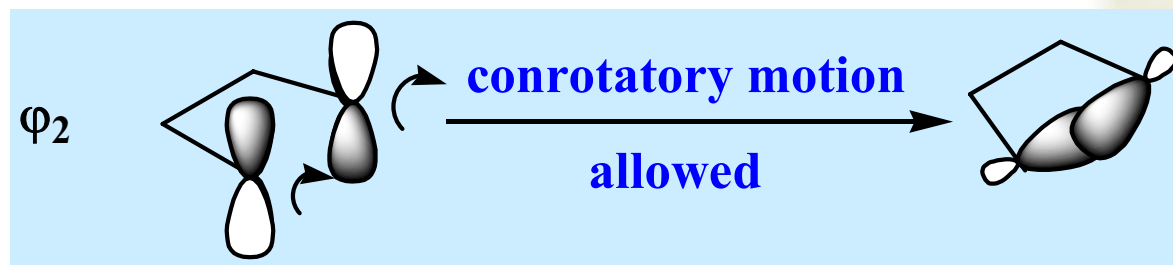


Reactions of either type are called *electrocyclic reactions*.

17.2.1 Electrocyclic Reactions of $4n$ π -Electron Systems

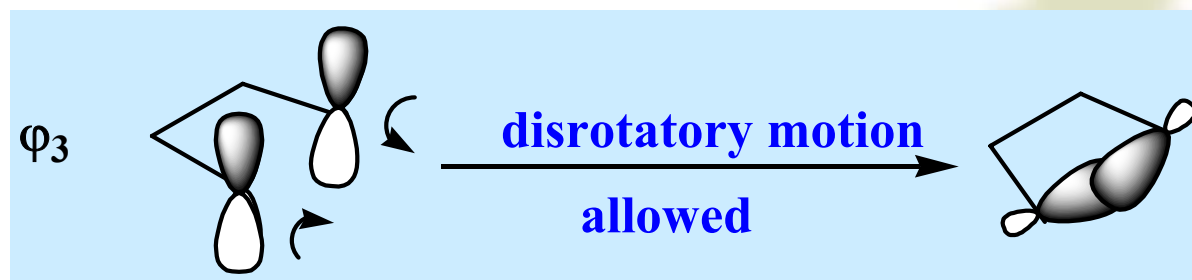
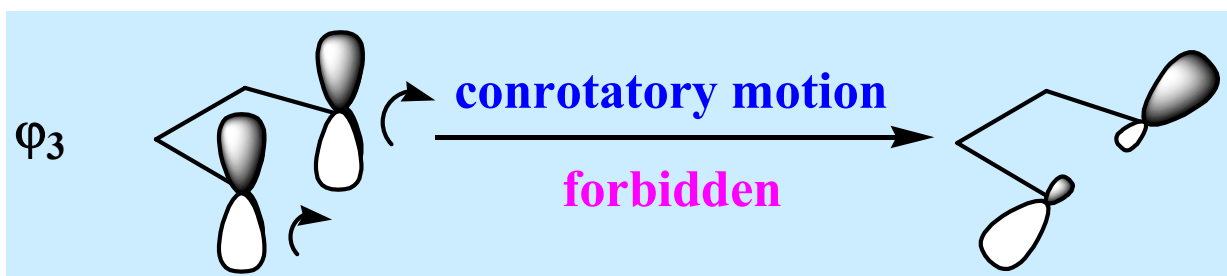
1. Thermal Electrocyclic Reaction:

热作用时，分子处于基态(the ground state)。当由丁二烯环化成环丁烯时由 ψ_2 (HOMO)参与成键。



2. Photochemical reaction:

光作用下，1,3-丁二烯分子将被激发。当由丁二烯环化成环丁烯时， ψ_3 由原来的LUMO轨道变为HOMO轨道，此时环化反应由 ψ_3 决定。



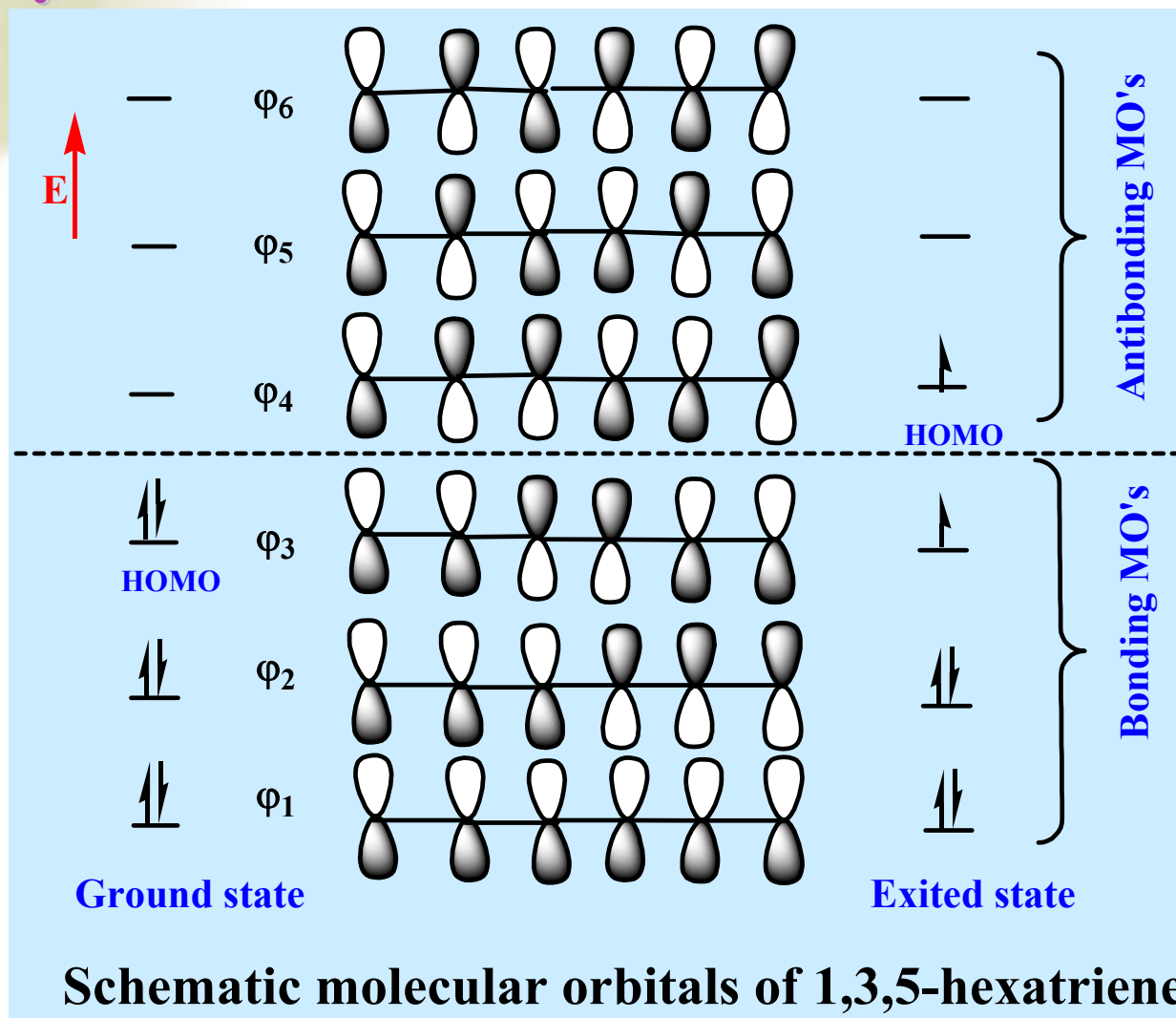
丁二烯含 $4n$ 个 π 电子，电环化的规律是：

加热 \rightarrow 顺旋，光照 \rightarrow 对旋。

The first Woodward-Hoffmann rule can be stated as follows:

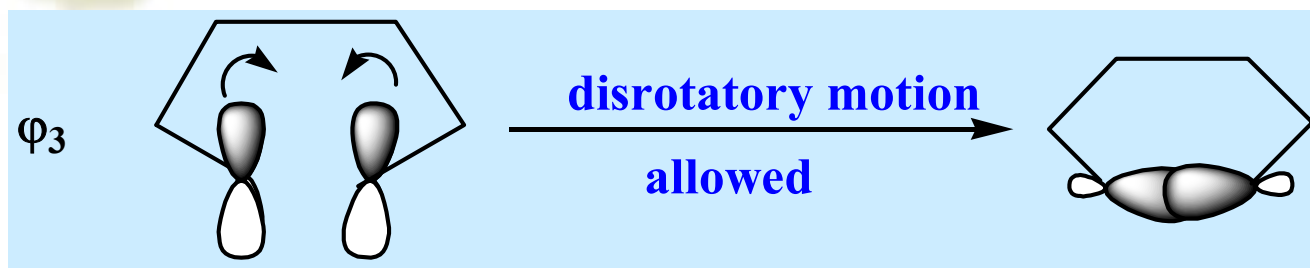
A thermal electrocyclic reaction involving $4n$ π electrons (where $n = 1, 2, 3, \dots$) proceeds with conrotatory motion; the photochemical reaction proceeds with disrotatory motion.

17.2.2 Electrocyclic Reactions of $(4n + 2)$ π -Electron Systems



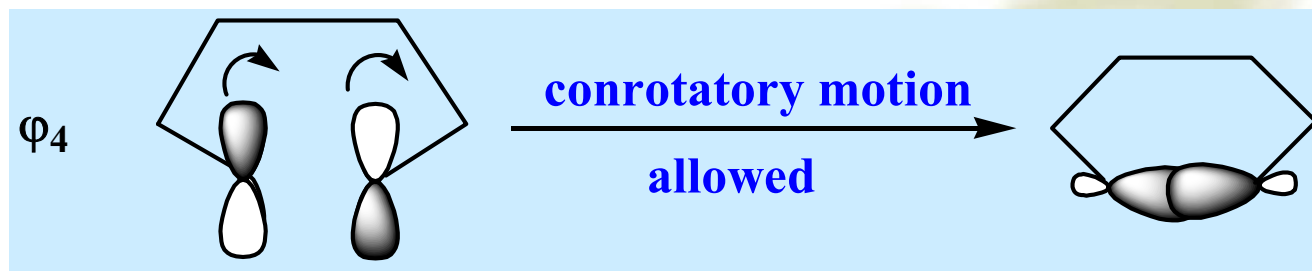
1. Thermal Electrocyclic Reaction:

己三烯基态时HOMO为 ψ_3 轨道。对旋是轨道对称性允许， C_1 ， C_6 间形成新的 σ 键。顺旋禁阻。



2. Photochemical reaction:

己三烯激发态时HOMO为 ψ_4 。对旋禁阻，顺旋允许。



己三烯含有 $4n + 2$ 个 π 电子，电环化反应的方式是：

加热 \rightarrow 对旋；光照 \rightarrow 顺旋。

The second Woodward-Hoffmann rule is stated as follows:

A thermal electrocyclic reaction involving $4n + 2 \pi$ electrons (where $n = 0, 1, 2, 3, \dots$) proceeds with disrotatory motion; the photochemical reaction proceeds with conrotatory motion.

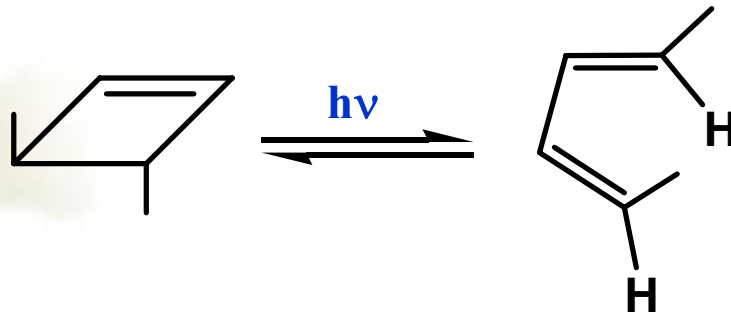
Conclusion:

电环化反应的空间过程取决于反应中开链异构物的HOMO的对称性。

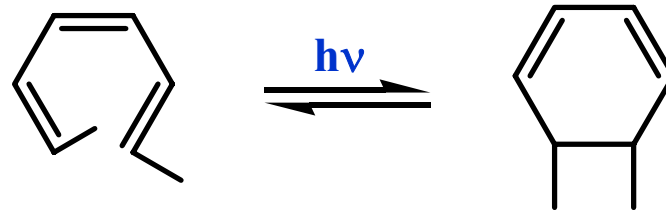
电环化反应的选择性可以归纳成下表:

π Electrons	Condition	Motion
$4n$	加热	顺旋
	光照	对旋
$4n + 2$	加热	对旋
	光照	顺旋

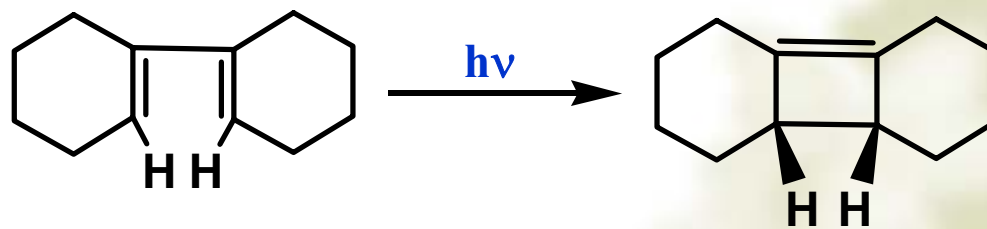
Ex
1:



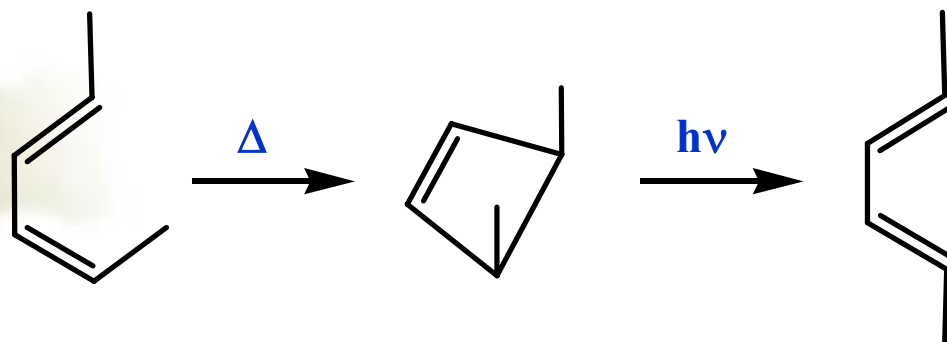
Ex 2:



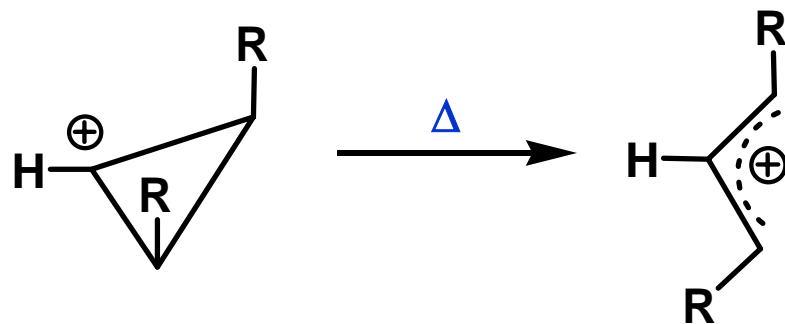
Ex 3:



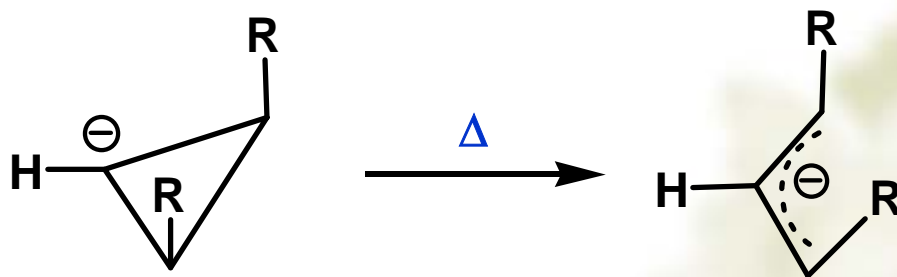
Ex 4:



Ex 5:



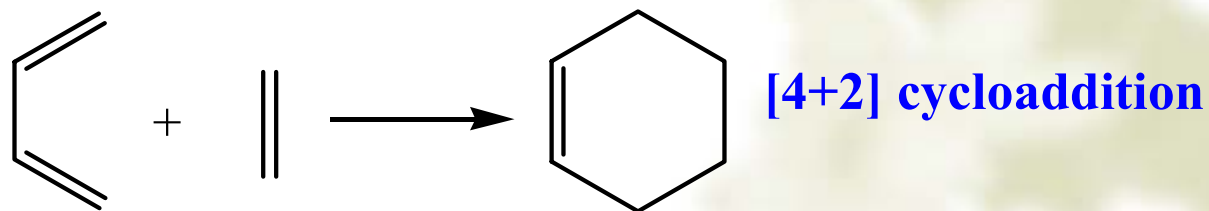
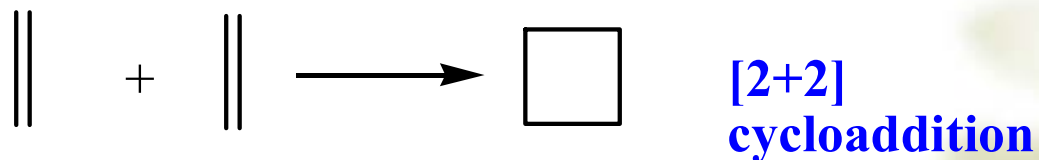
Ex 6:



17.3 CYCLOADDITION REACTIONS

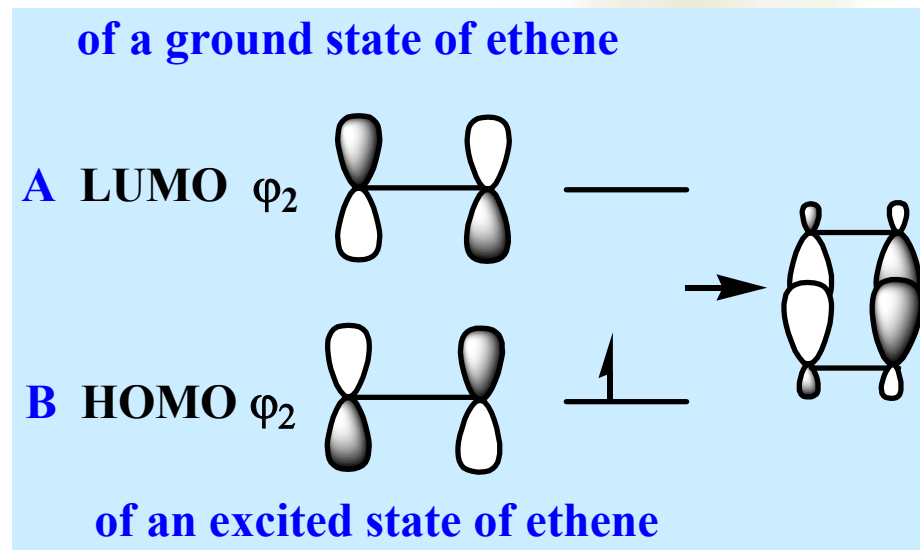
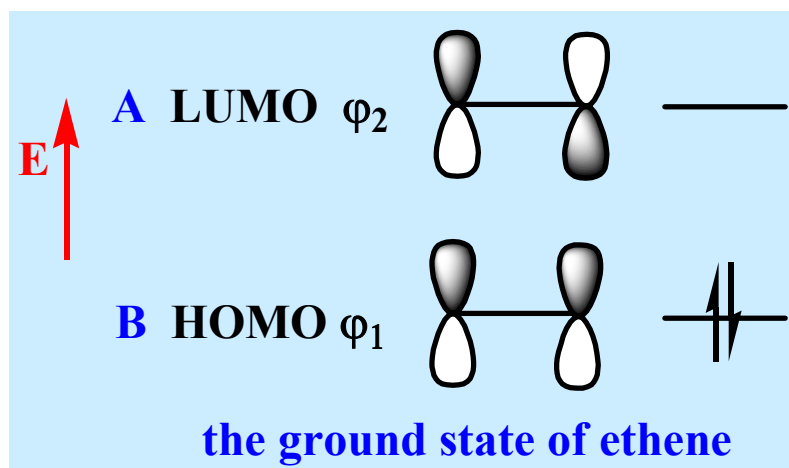
Definition:

There are a number of reactions of alkenes and polyenes in which **two molecules react to form a cyclic product**. These reactions, called *cycloaddition reactions*, are shown next.

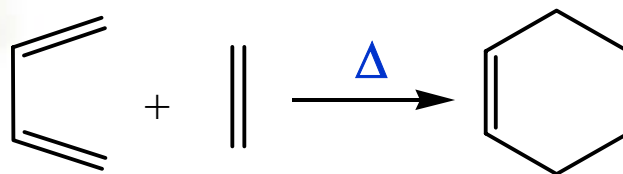


环加成和环分解互为逆反应，他们遵守同一规律。从FMO观点可以分析环加成反应：从能量上考虑，在双分子反应中起决定作用的FMO为一分子的HOMO和另一分子的LUMO。

17.3.1 [2+2] Cycloaddition Reactions

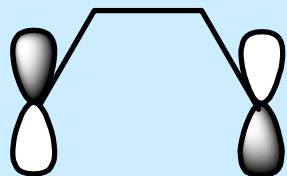


17.3.2 [4+2] Cycloaddition Reactions

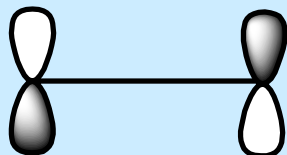


of a ground state of butadiene

HOMO φ_2



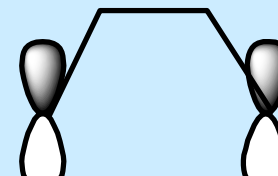
LUMO φ_2



of a ground state of ethene

of a ground state of butadiene

LUMO φ_3



HOMO φ_1

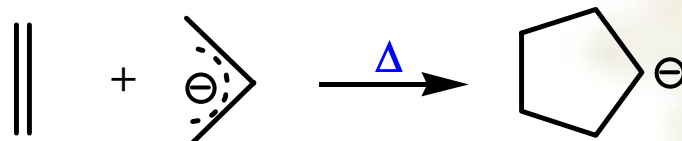
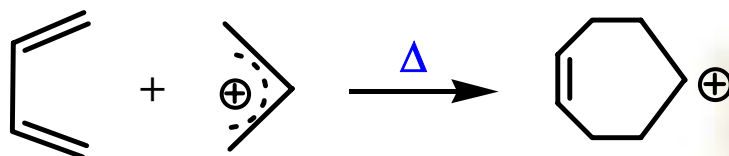
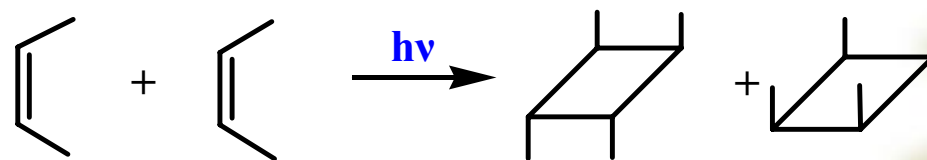


of a ground state of ethene

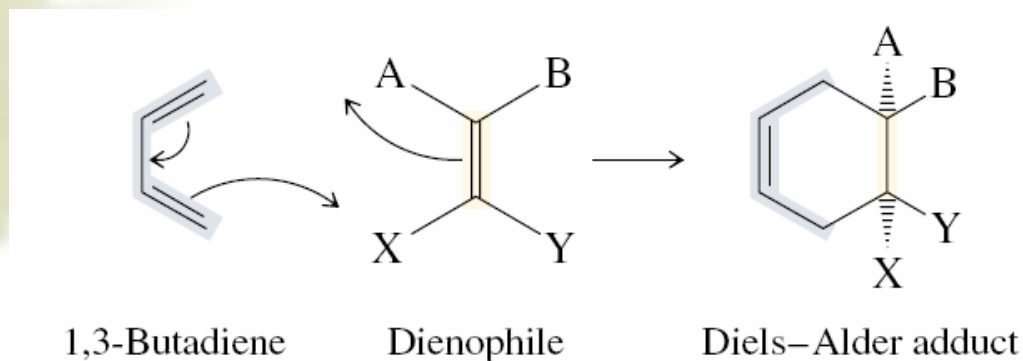
Conclusion

$k_1 + k_2 \pi$ -Electrons	Condition	Symmetry
$4n + 2$	热	允许
	光	禁阻
$4n$	光	允许
	热	禁阻

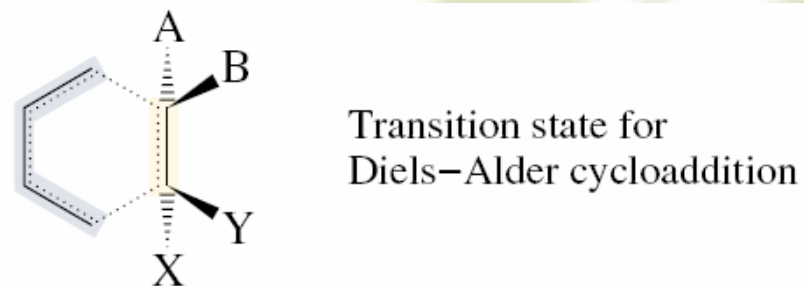
Ex 1:



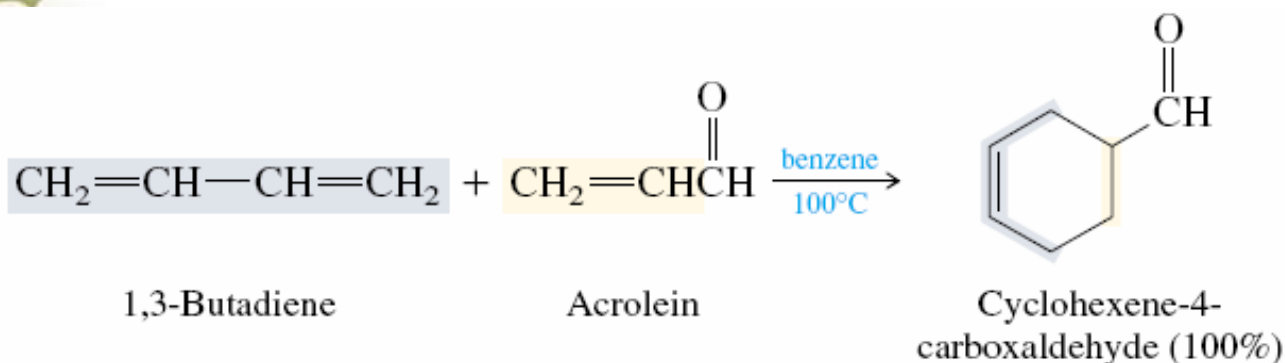
Diels-Alder Reaction:



Bond formation occurs at both ends of the diene system, and the Diels-Alder transition state involves a cyclic array of six carbons and six electrons. The diene must adopt the *s-cis* conformation in the transition state.

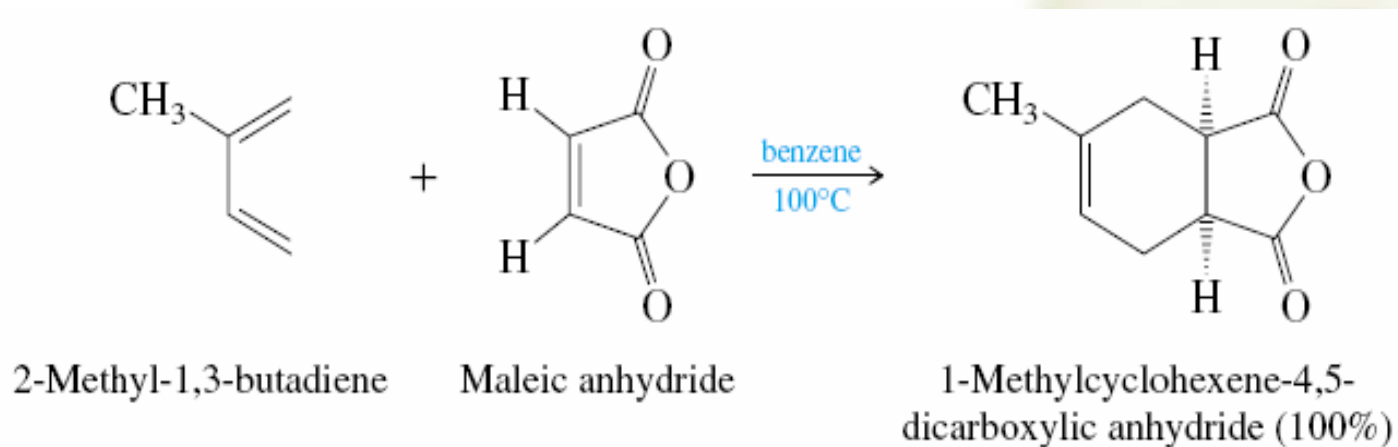


Ex 2:



The product of a Diels-Alder cycloaddition always contains one more ring than was present in the reactants.

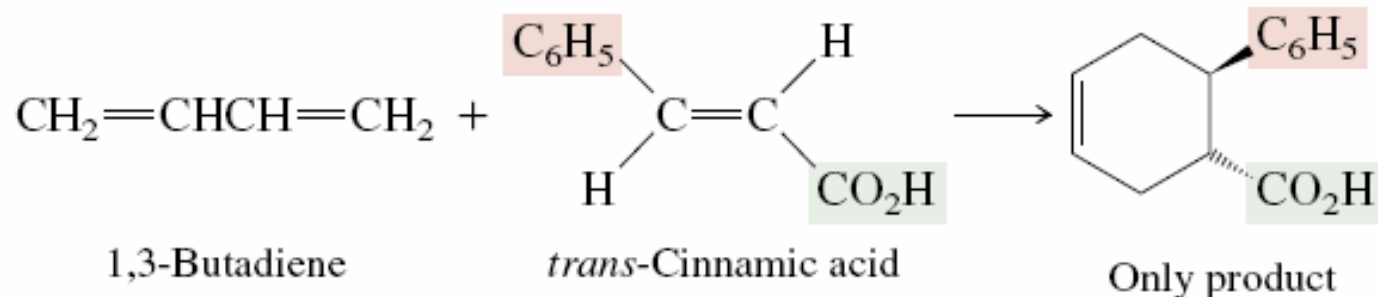
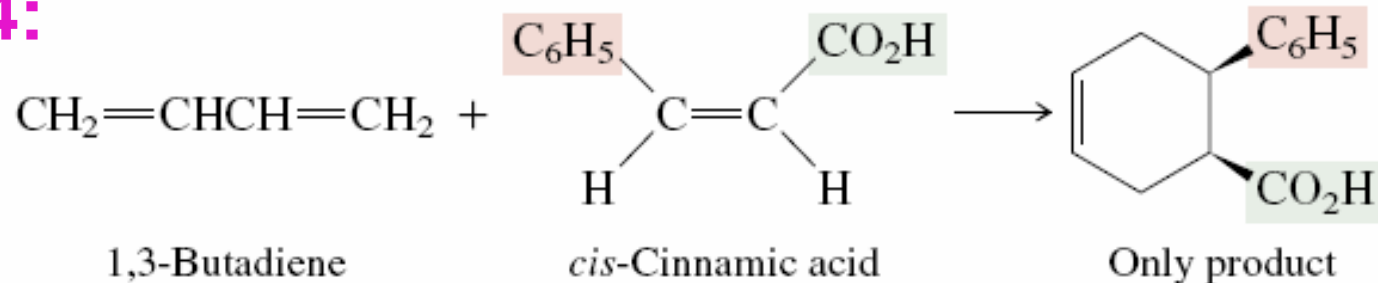
Ex 3:



The Diels-Alder reaction is stereospecific.

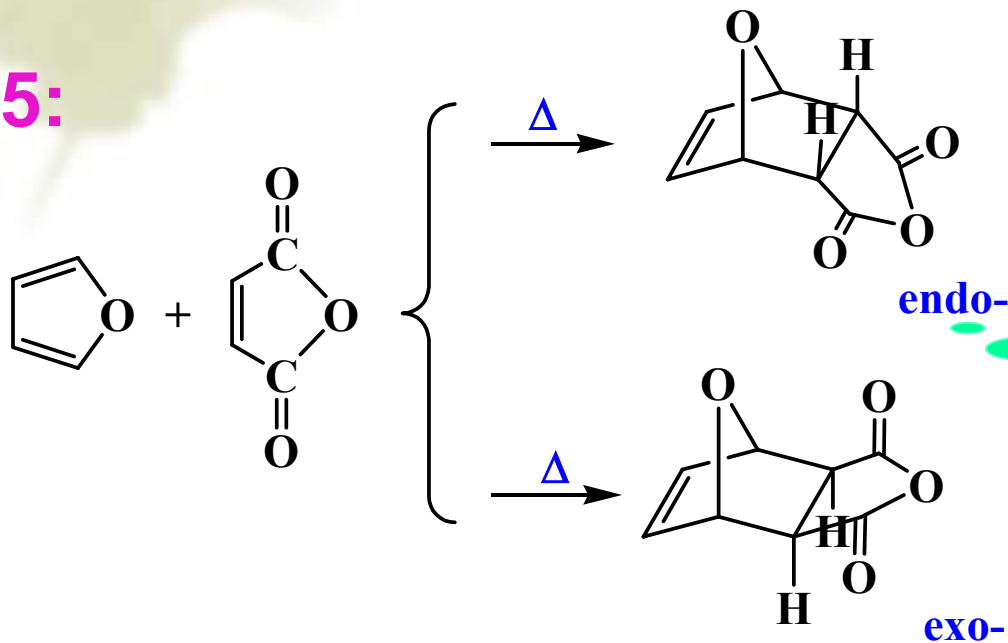
Substituents that are *cis* in the dienophile remain *cis* in the product; substituents that are *trans* in the dienophile remain *trans* in the product.

Ex 4:



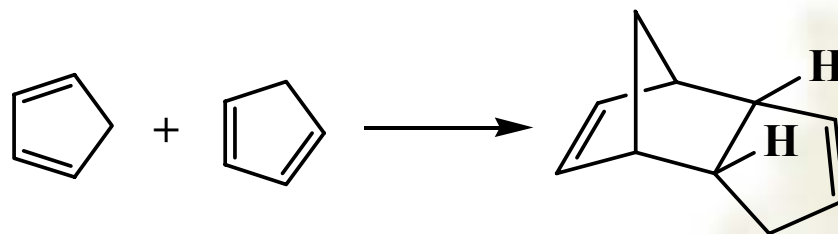
Cyclic dienes yield bridged bicyclic Diels-Alder adducts.

Ex 5:

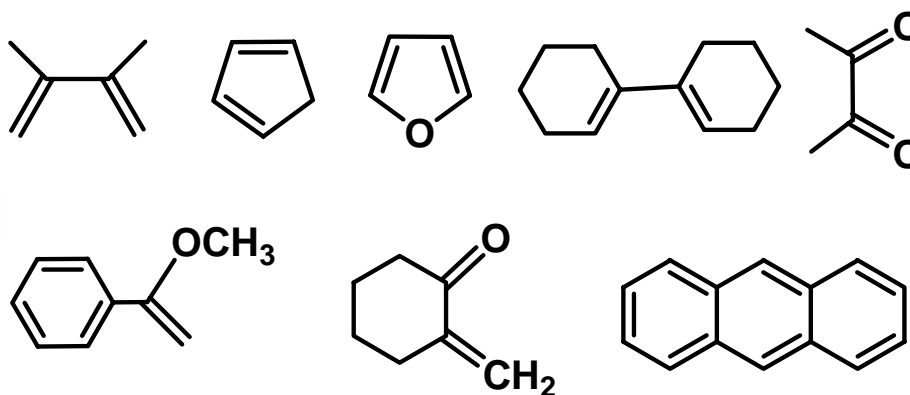


The main product

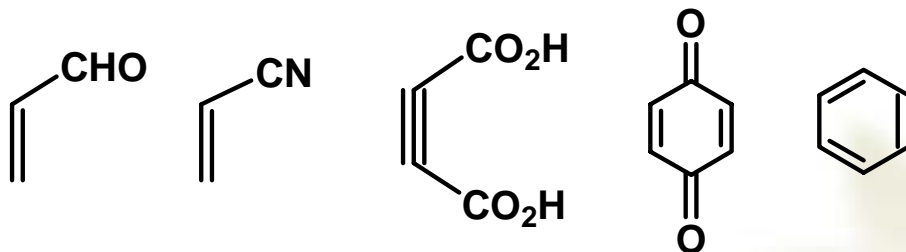
Ex 6:



Diene

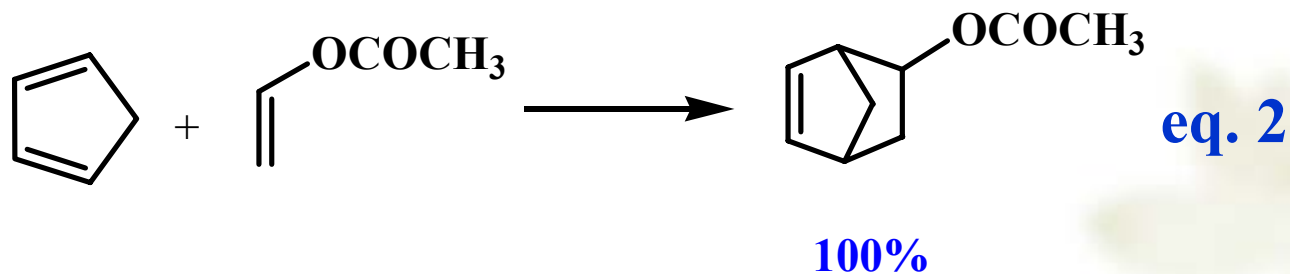
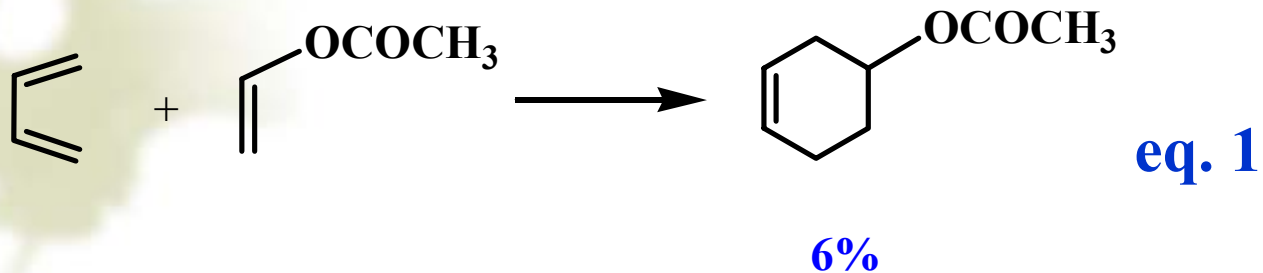


Dienophile



The importance of the Diels-Alder reaction is in synthesis. It gives us a method to form *two* new carbon-carbon bonds in a single operation and requires no reagents, such as acids or bases, that might affect other functional groups in the molecule.

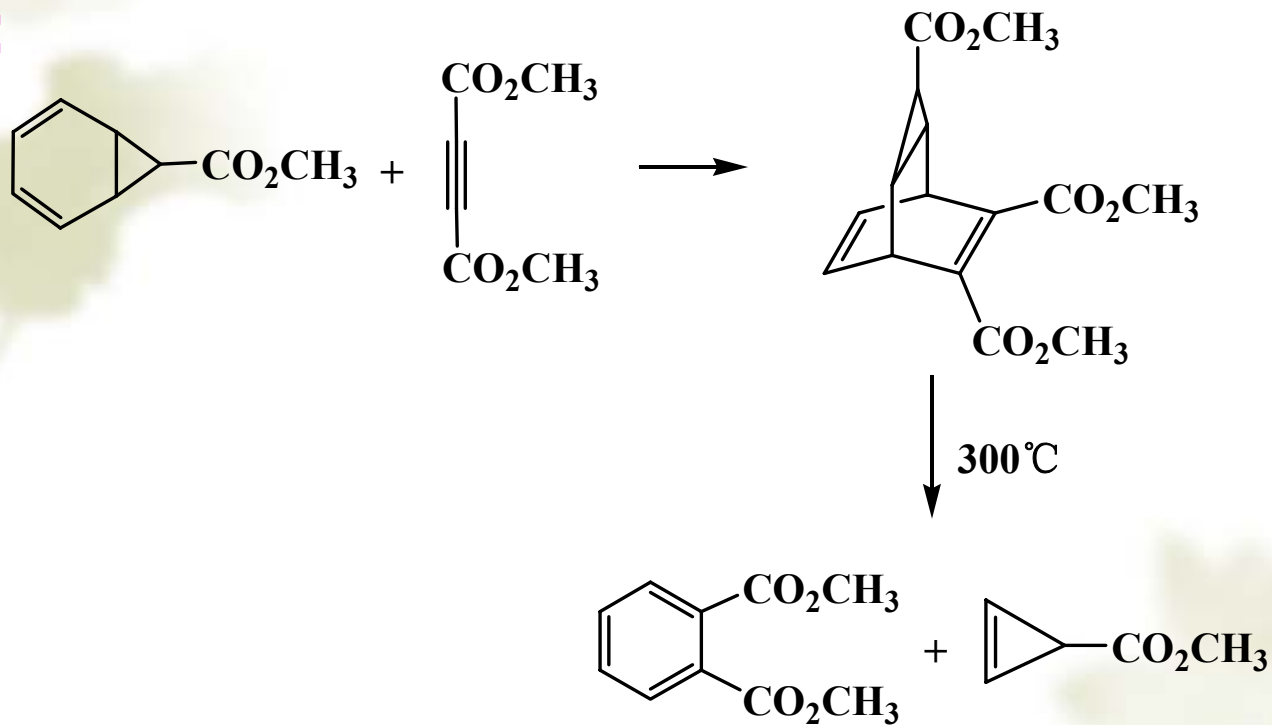
Ex 7:



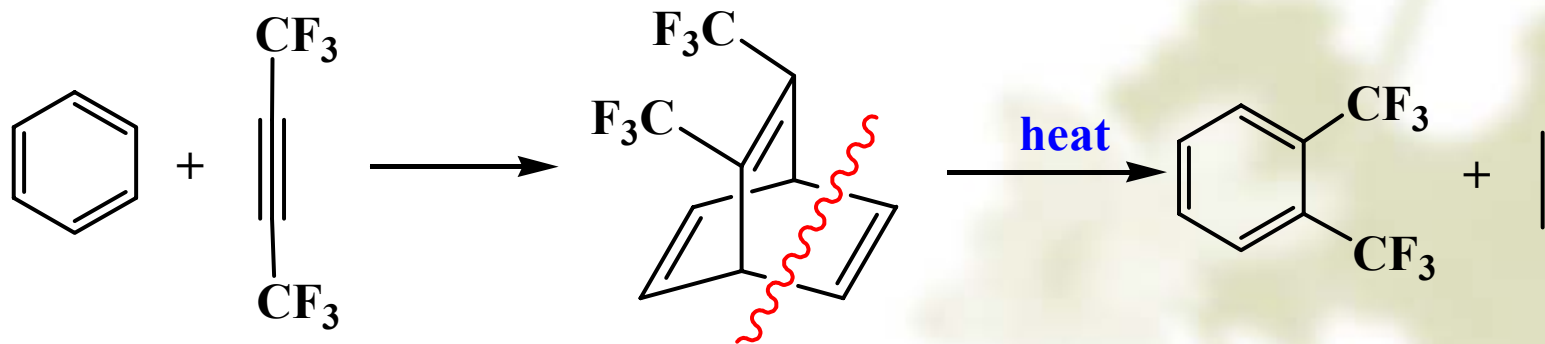
比较1和2发现：环状二烯体的反应活性大于开链的。

Why?

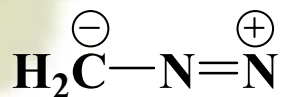
Ex 8:



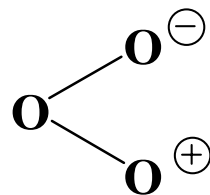
Ex 9:



17.3.3 1,3-Dipole Addition Reaction

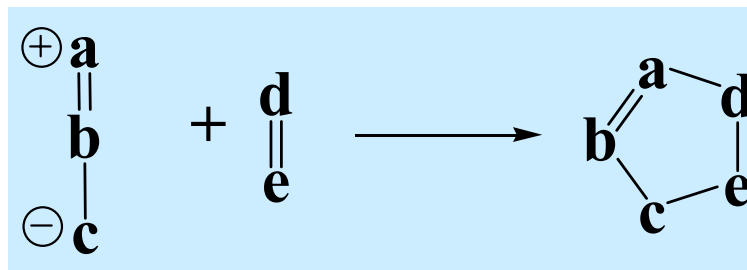


Diazomethane



Ozone

General formula:



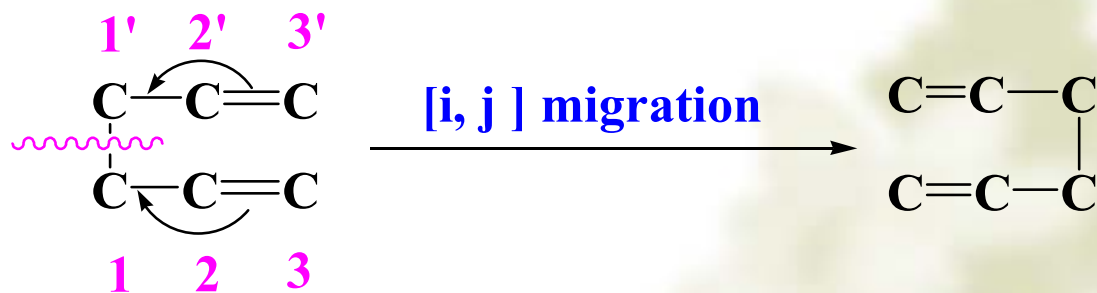
这类反应是合成五元杂环的方法。

Ex: P.200 11-3

17.4 σ BOND MIGRATION REACTIONS

Definition: 一个碳原子上的 σ 键迁移到另一个碳原子上，随之共轭链发生转移的反应称为 σ 迁移反应。

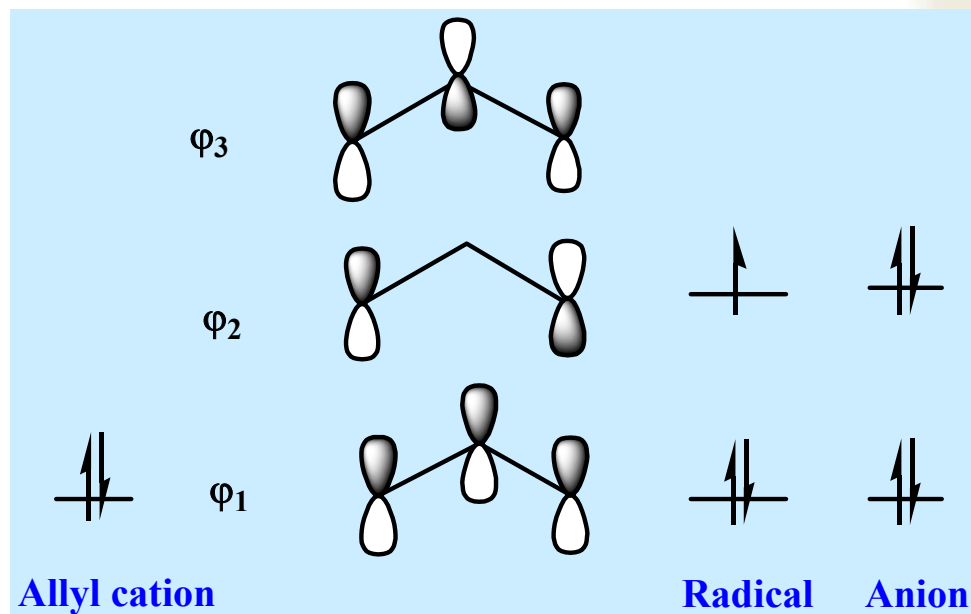
Classification of σ bond migration reactions:



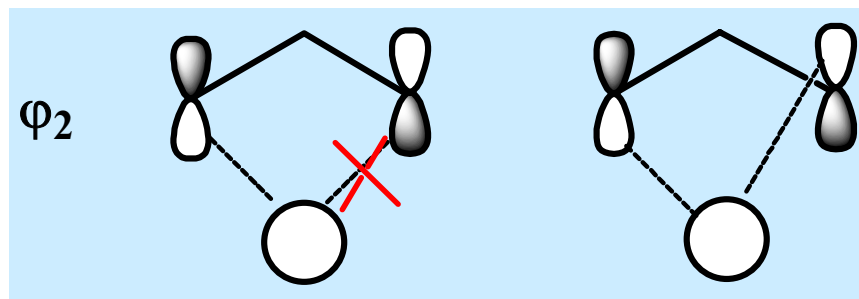
17.4.1 [1, j] Migration of H Atom

从几何构型来看， σ 键迁移反应可分为两种类型：一种是同面反应，迁移前后的 σ 键在共轭平面同一侧；另一种是异面反应，迁移前后的 σ 键在共轭平面的两侧。

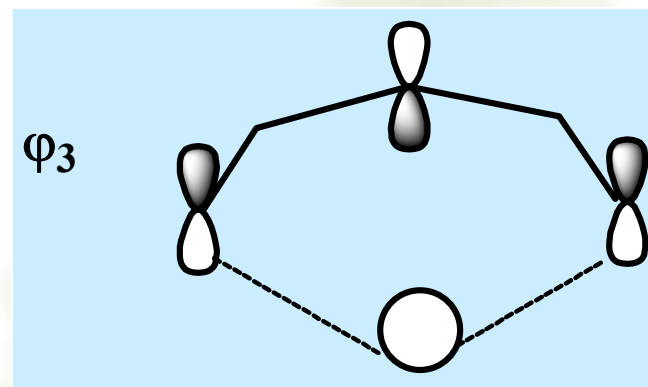
Ex: 以[1, 3]氢迁移为例，



在发生[1,3]氢迁移时，如果体系中有一对 π 电子和一对 σ 电子，那么HOMO是 ψ_2 ，同面迁移禁阻，异面迁移允许。



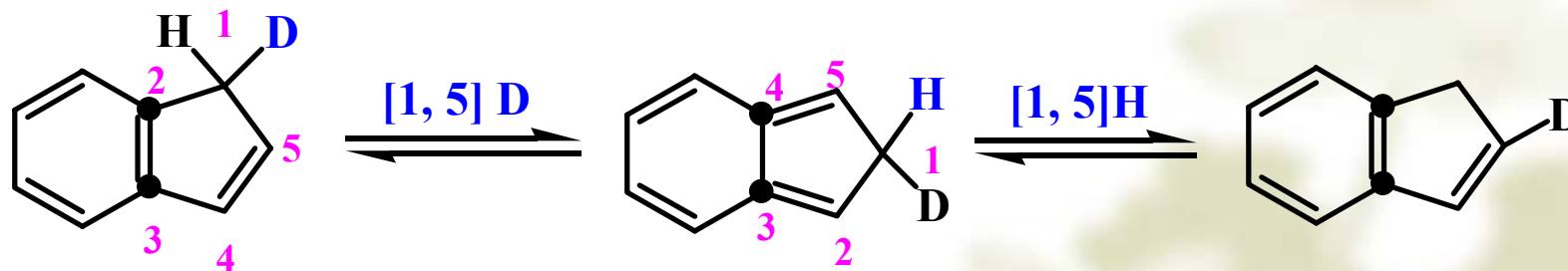
如果体系多一个 π 键，即[1,5]氢迁移时，HOMO为 ψ_3 轨道，将同面迁移允许。



Conclusion:

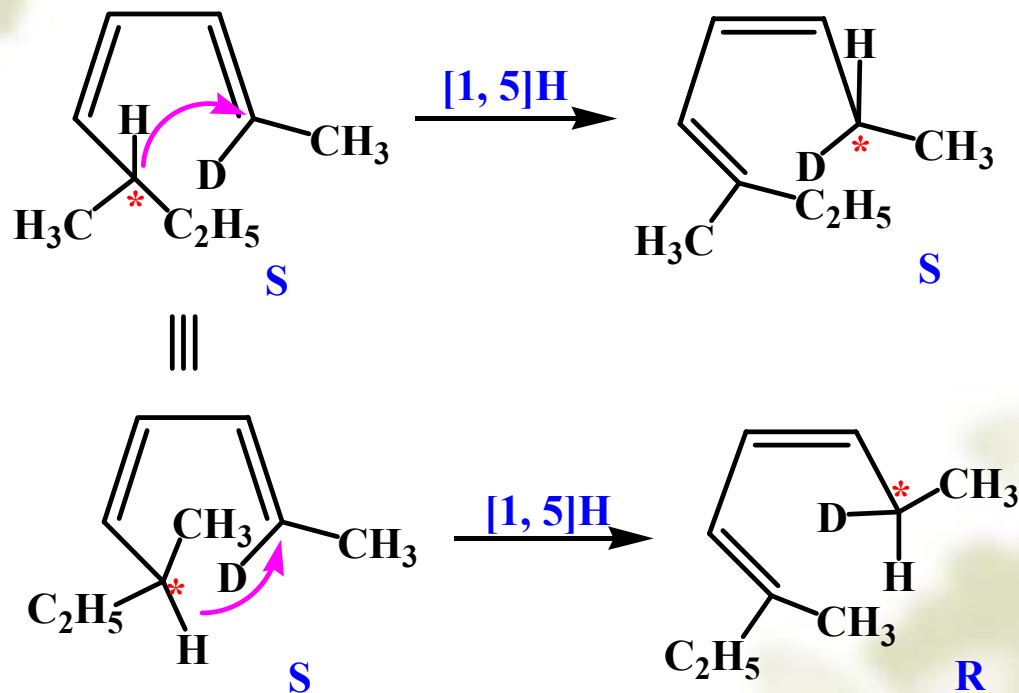
[1, 5] H迁移是同面迁移允许，且活化能小，容易进行；[1, 3]和[1, 7] H迁移是异面迁移允许，但活化能大，较难进行。因此，[1, 5] σ 键绝对优先于[1, 3]和[1, 7] σ 键迁移。

Ex:



同面迁移或异面迁移的直接结果导致了分子中手性原子的构型变化。

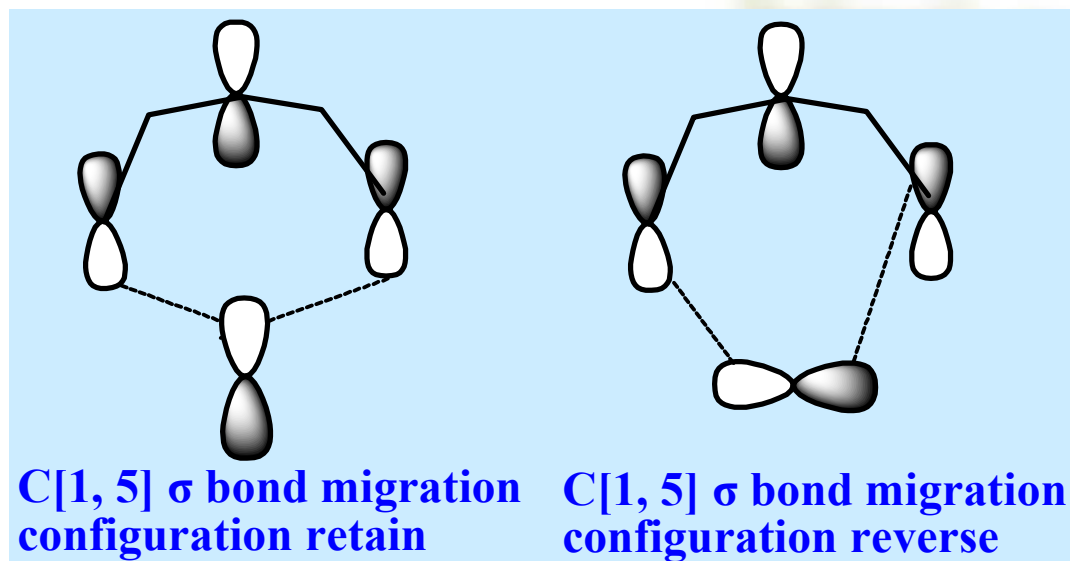
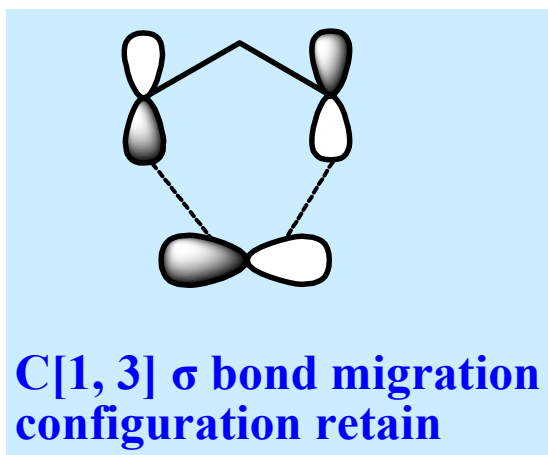
Ex:



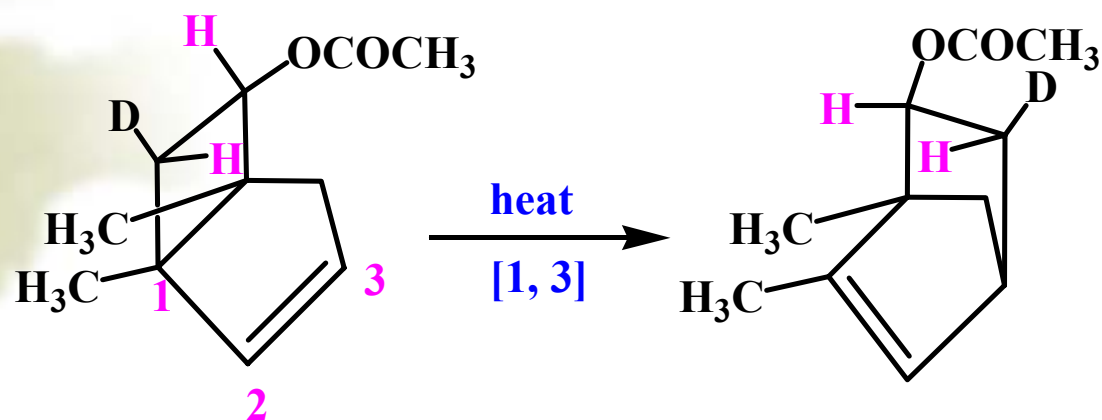
17.4.2 [1, j] Migration of Carbon Atom

根据轨道对称性的要求，[1,3]C迁移——同面 / 反转 允许；[1,5]C迁移——同面/保留 允许，异面/反转 允许。

用轨道示意图表示如下：



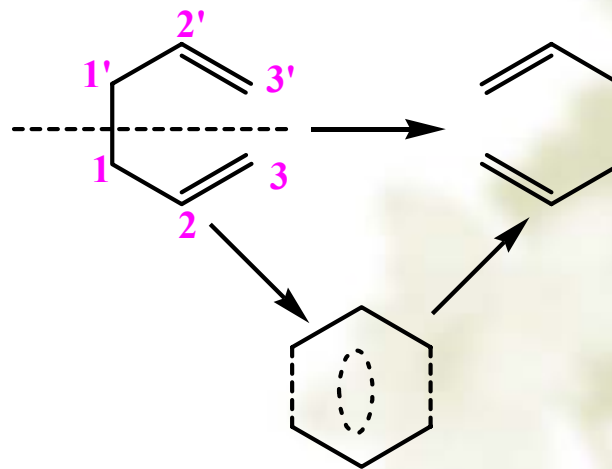
Ex:



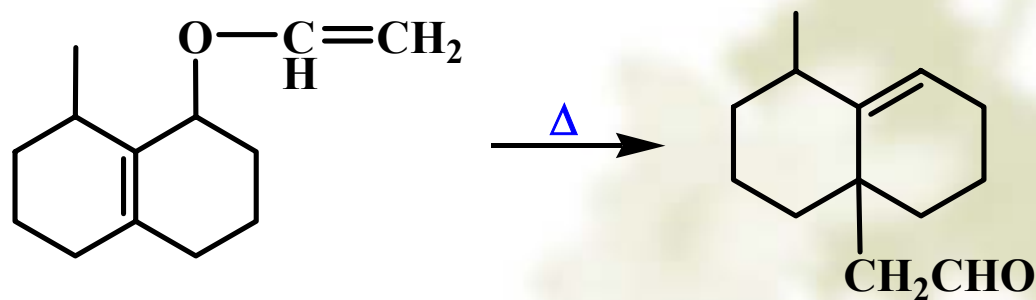
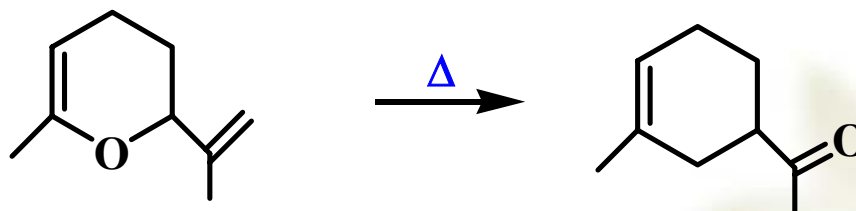
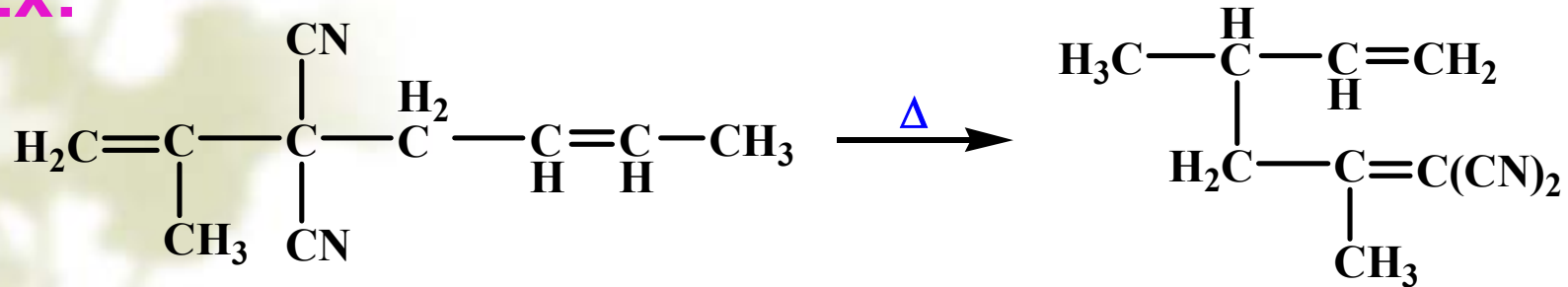
[1,3]C迁移, 同面/反转允许

17.4.3 [3, 3] σ Bond Migration

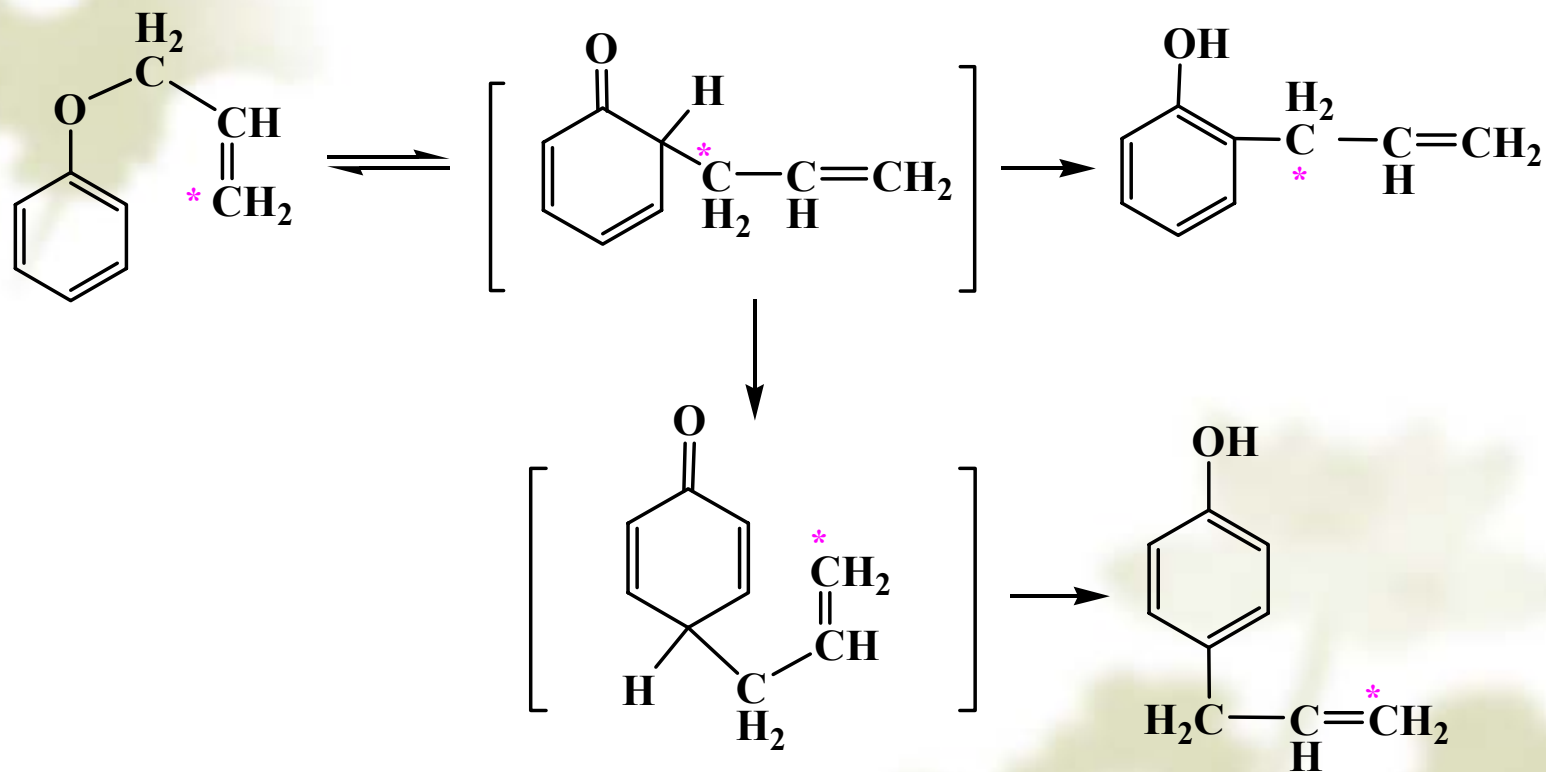
1. Cope Reaction:



Ex:

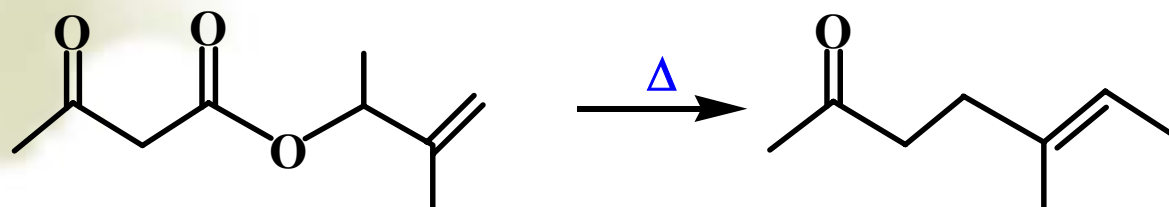


2. Claisen Rearrangement:



如果邻位被占据，得到的全是对位产物

Problem:



Solution:

