



TÁMOP-4.1.1.F-14/1/KONV-2015-0006

SZTE TTIK, KTCS, 1a) Duális és moduláris  
képzésfejlesztés a mesterképzéshez

## Periciklusos reakciók 3: szigmatróp átrendeződések

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020



MAGYARORSZÁG  
KORMÁNYA

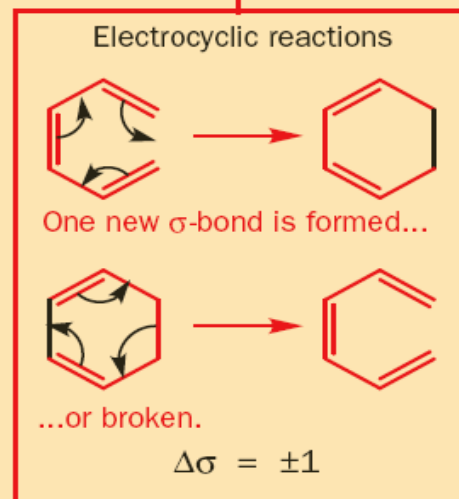
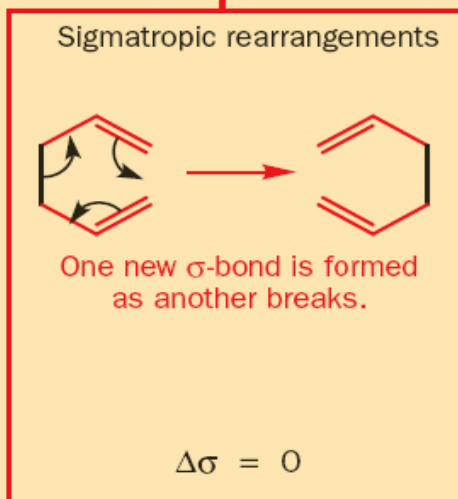
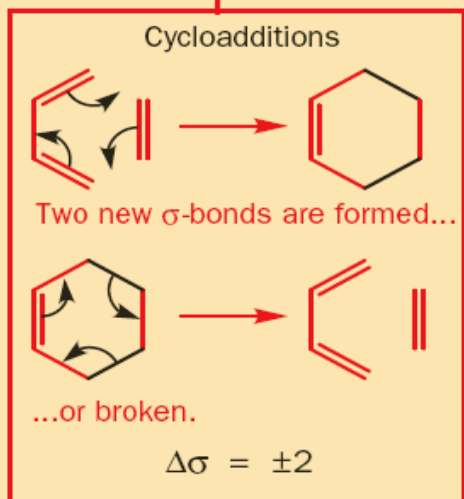
Európai Unió  
Európai Szociális  
Alap



BEFEKTETÉS A JÖVŐBE

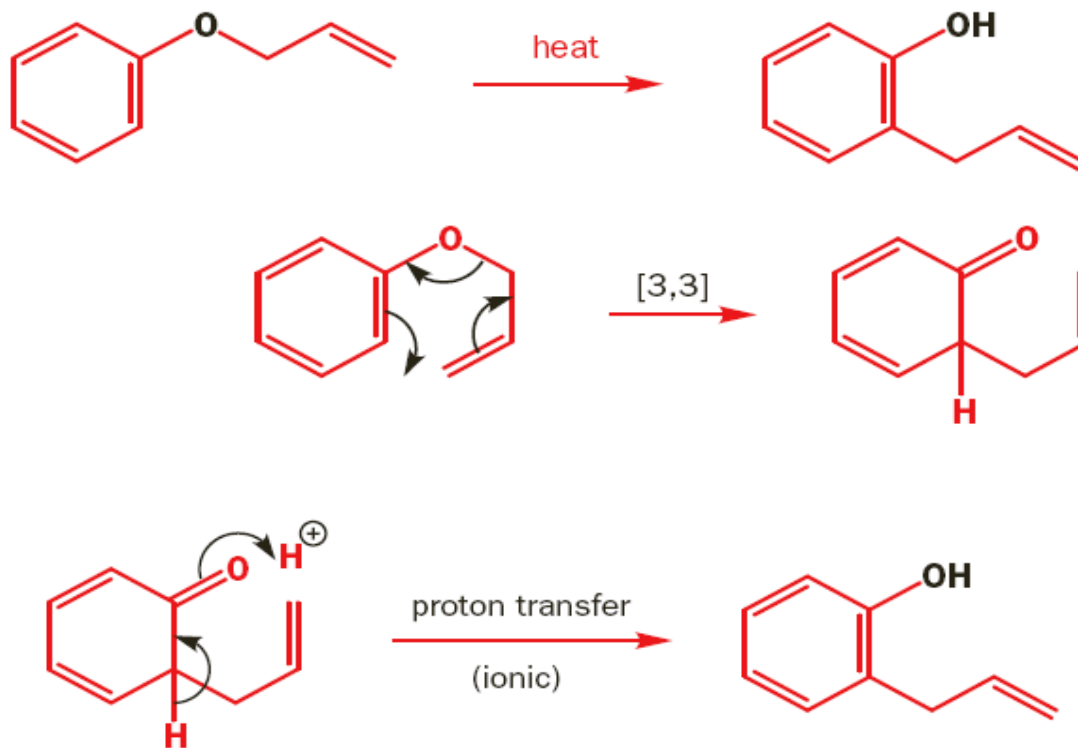
- The types of pericyclic reactions are distinguished by the number of  $\sigma$  bonds made or broken

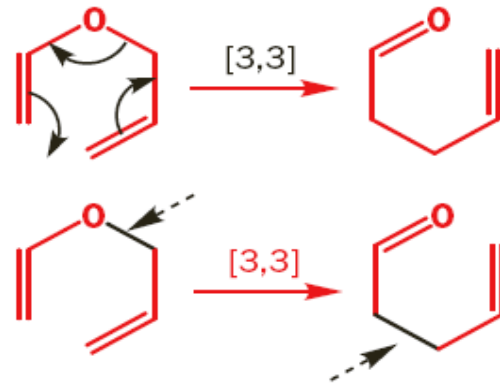
Types of pericyclic reactions

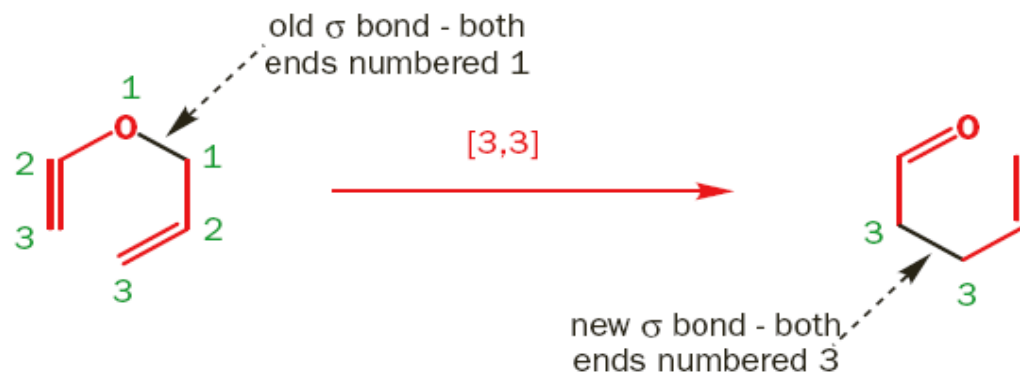


# **[3,3] szigmatróp átrendeződések**

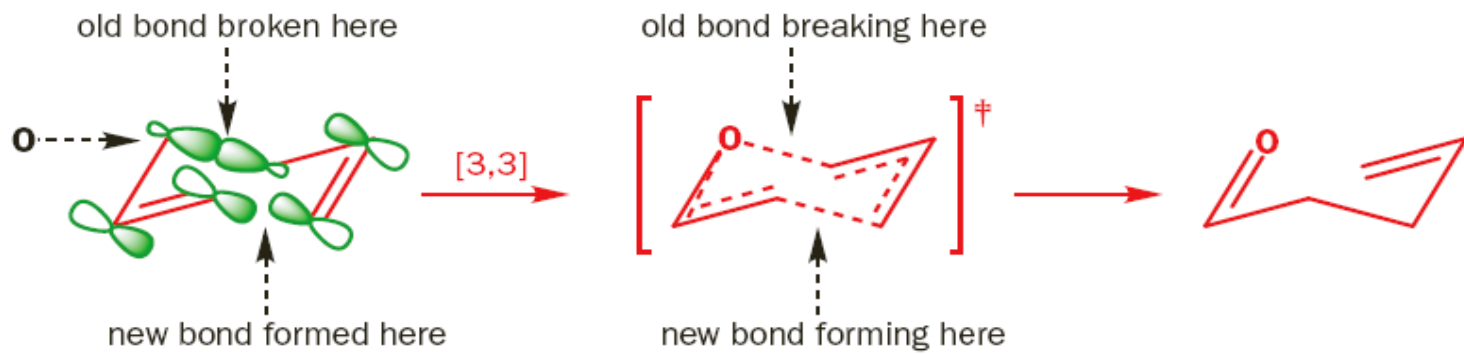
# Claisen-átrendeződés



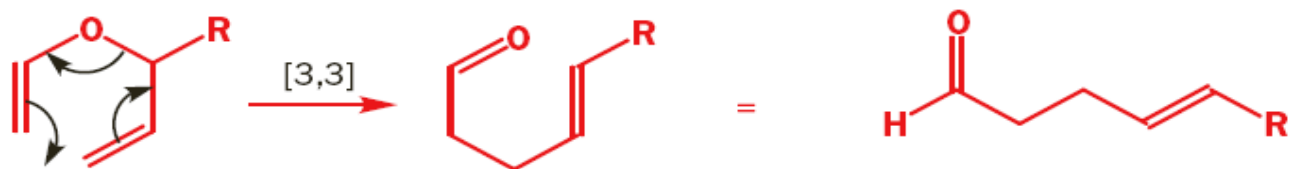




# **Értelmezés a frontális molekulapálya modell alapján**





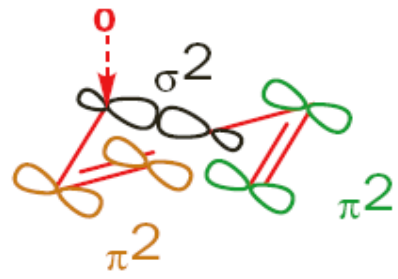


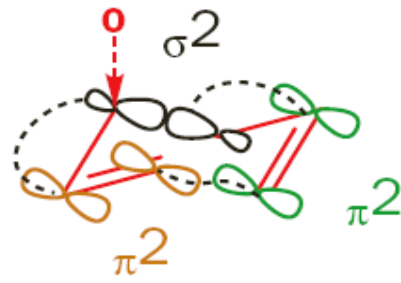
az átmeneti komplexben az R-csoport ekvatoriális helyzetben szeret lenni – ez pedig preformált transz konfigurációt jelent

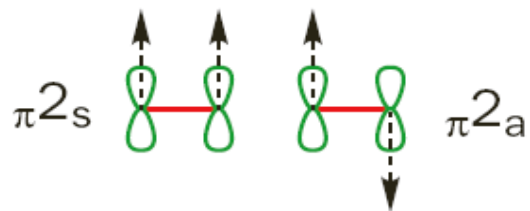
# **Értelmezés a Woodward-Hoffmann modell alapján**

● **Woodward–Hoffmann rules**

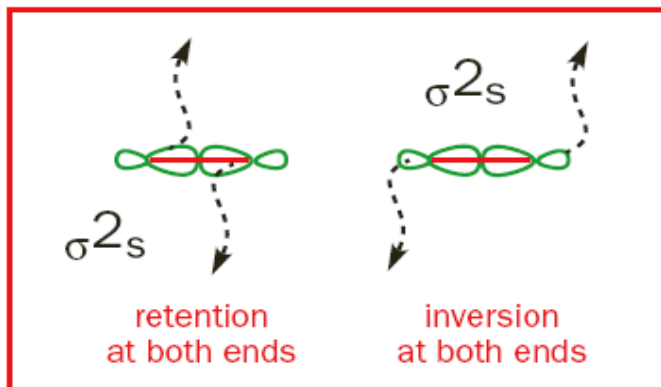
In a thermal pericyclic reaction the total number of  $(4q + 2)_s$  and  $(4r)_a$  components must be odd.



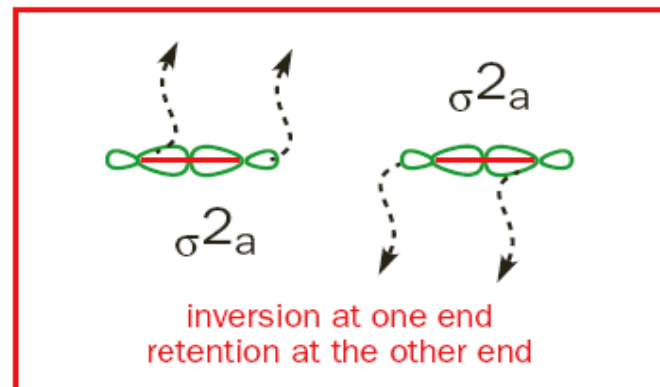


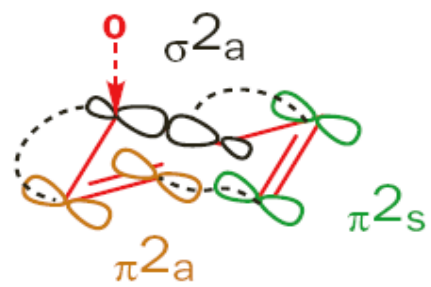
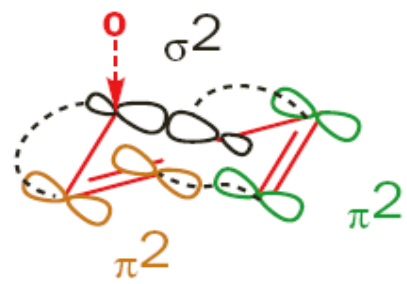


s bond reacting suprafacially

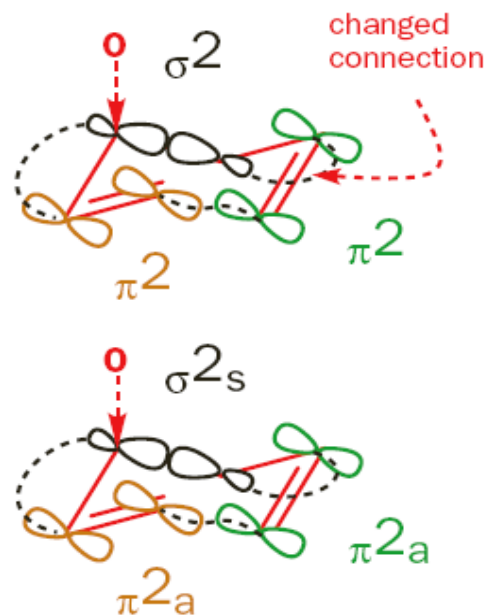


s bond reacting antarafacially





vagy



number of  $(4q + 2)_s$  components: 1

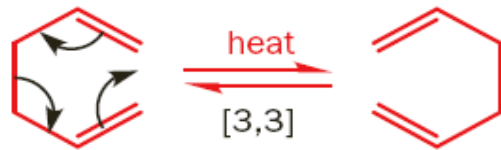
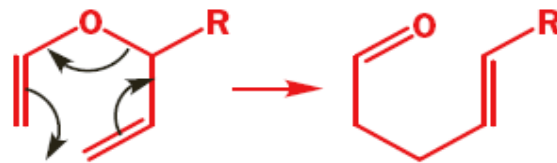
number of  $(4r)_a$  components: 0

sum = 1

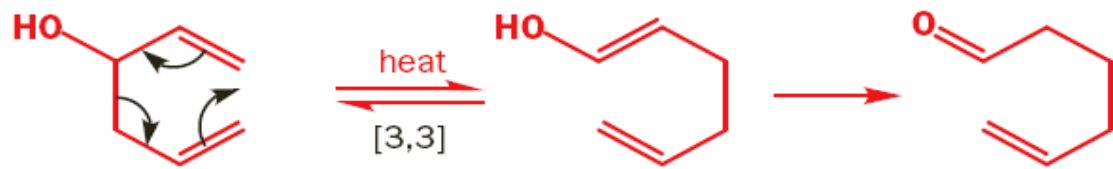
so reaction is allowed thermally

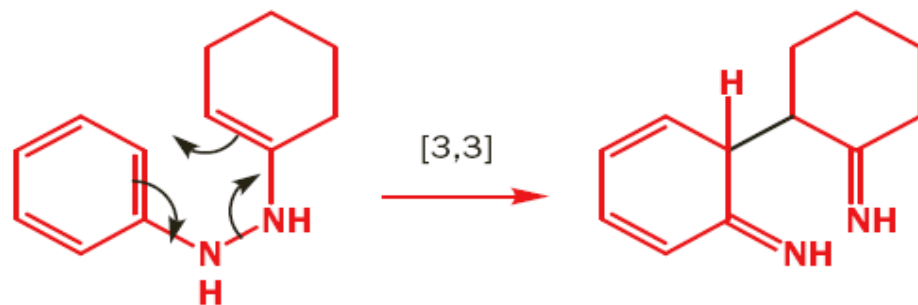
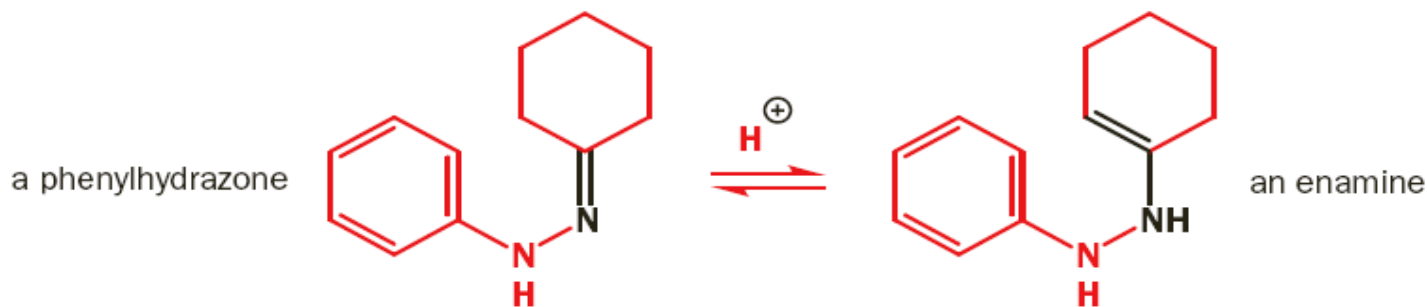
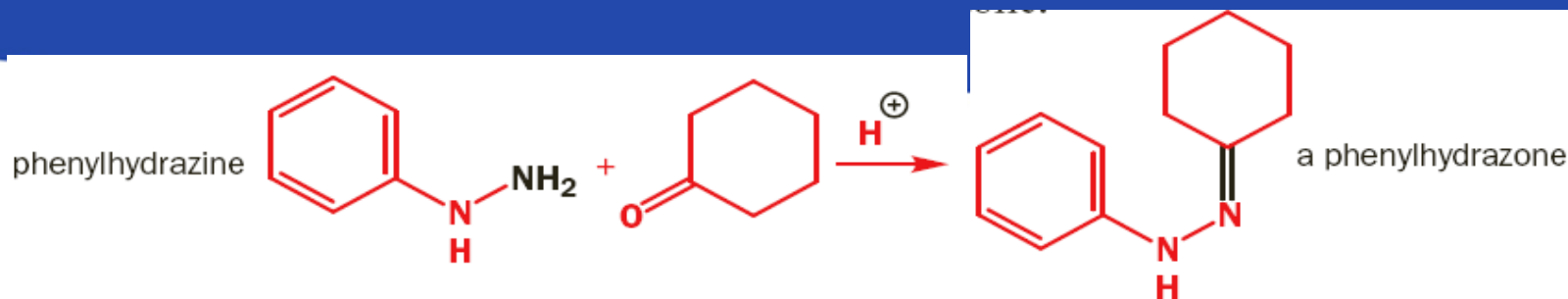


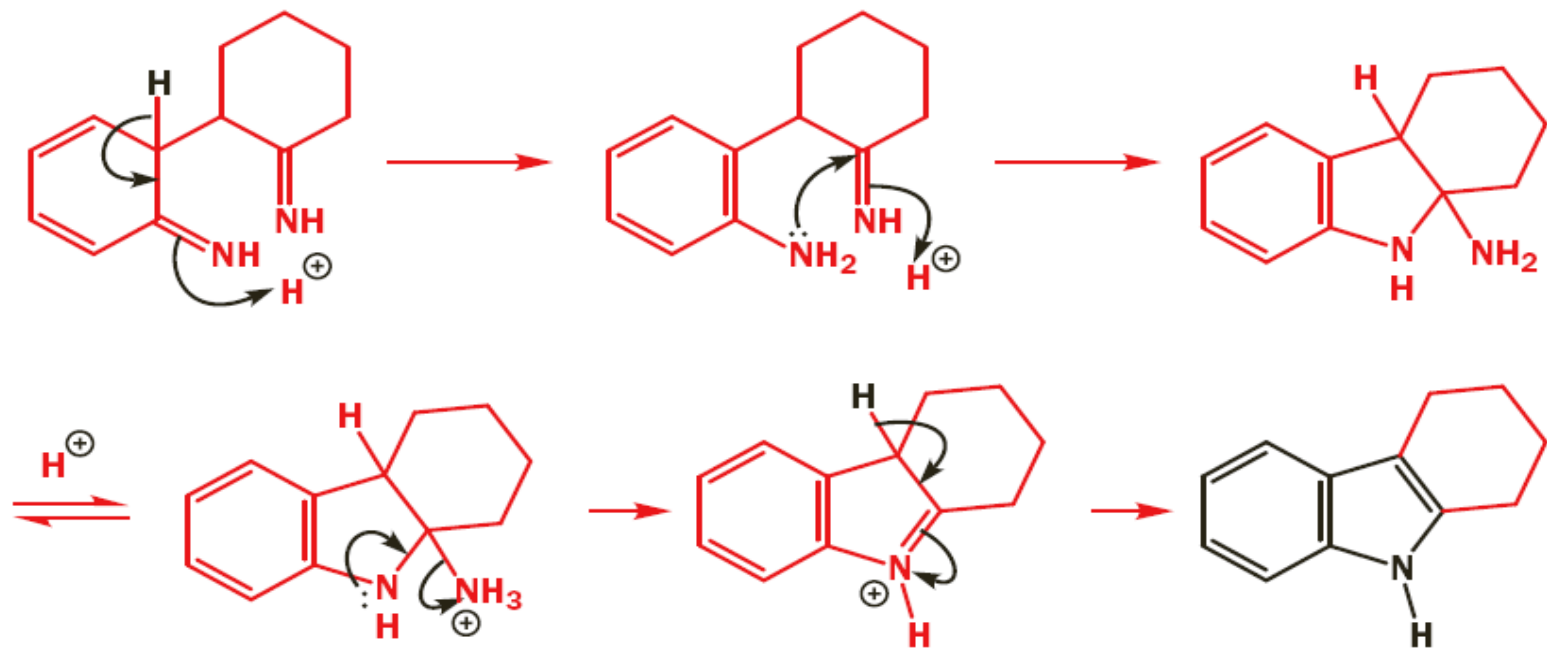
## Claisen-átrendeződés



## Cope-átrendeződés



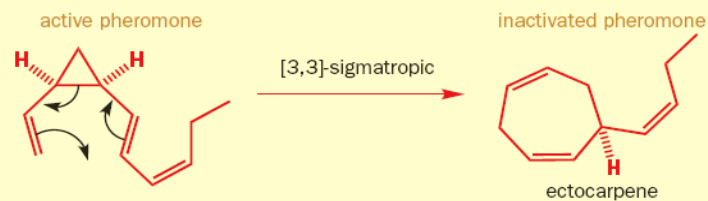




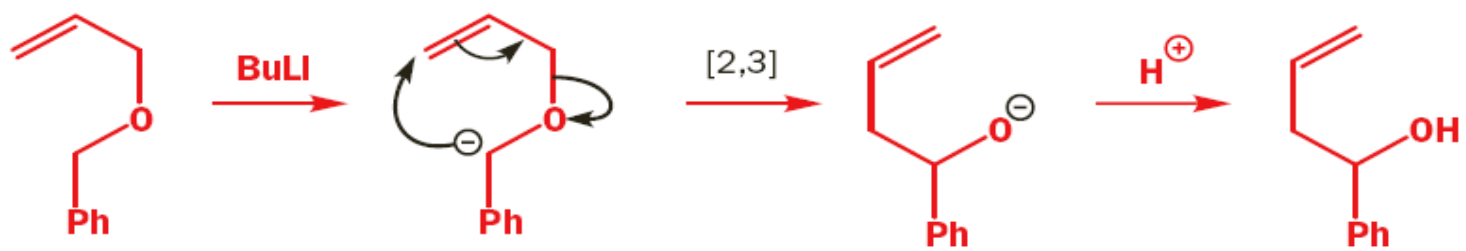
## Sex for seaweeds censored by a [3,3]-sigmatropic rearrangement

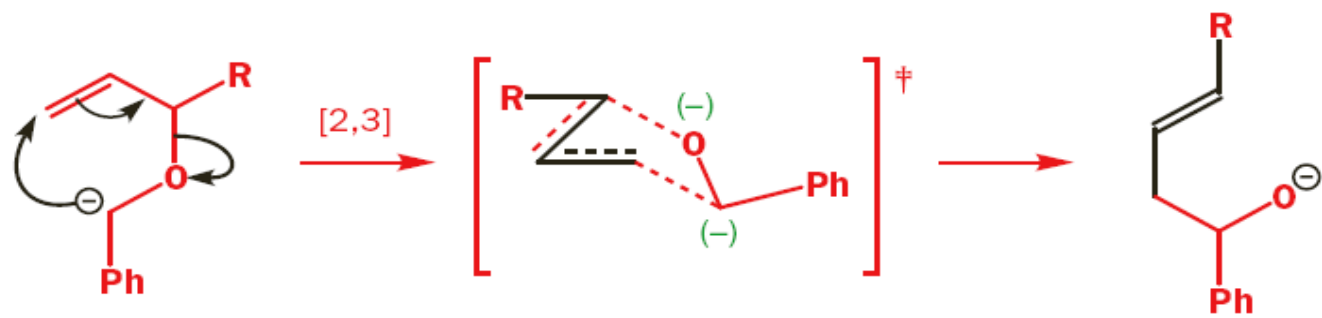
In order to reproduce, the female gametes of marine brown algae must attract mobile male gametes. This they do by releasing a pheromone, long thought to be the cycloheptadiene ectocarpene. In 1995 results were published that suggested that, in fact, the pheromone was a cyclopropane, and that ectocarpene was ineffective as a pheromone

How had the confusion arisen? Well, the remarkable thing is that the cyclopropyl pheromone inactivates itself, with a half-life of several minutes at ambient temperature, by [3,3]-sigmatropic rearrangement to the cycloheptadiene, driven by release of strain from the three-membered ring. This not only confused the earlier pheromone chemists, but it also provides a marvellously precise way for the algae to signal their presence and readiness for reproduction without saturating the sea water with meaningless pheromone.



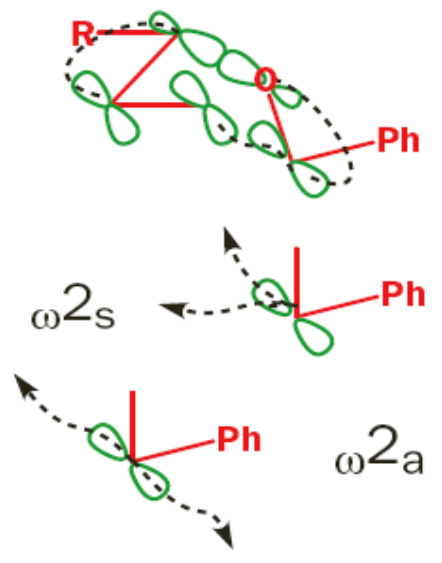
## **[2,3] szigmatróp átrendeződések**





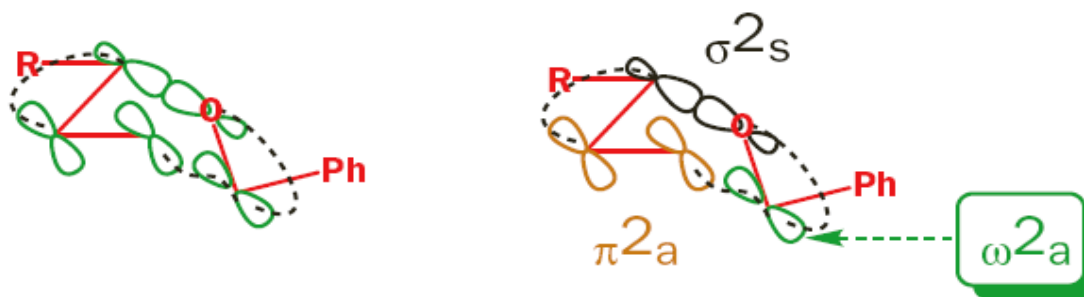


# **Értelmezés a Woodward-Hoffmann modell alapján**

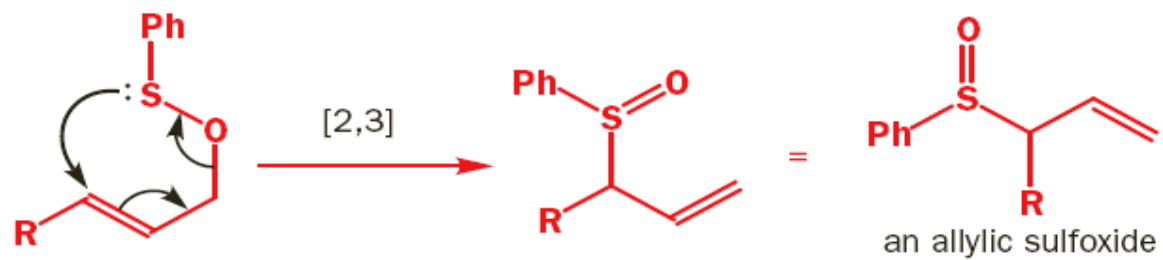
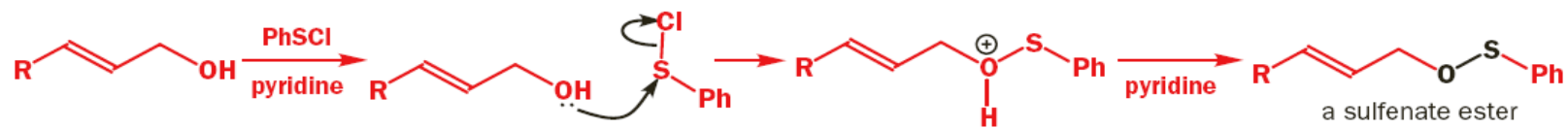


## ● Woodward–Hoffmann rules

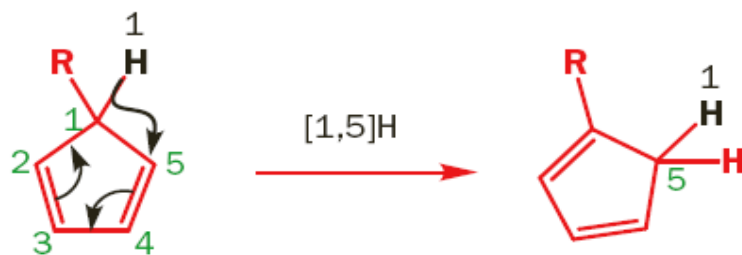
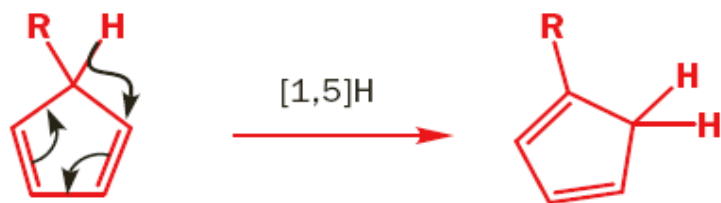
In a thermal pericyclic reaction the total number of  $(4q + 2)_s$  and  $(4r)_a$  components must be odd.



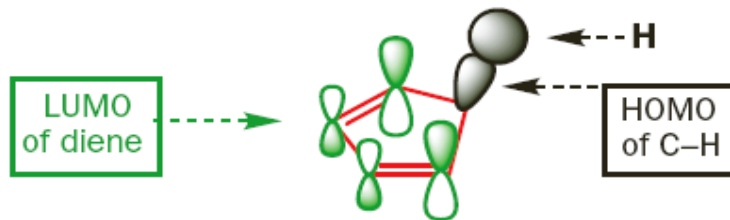
a [2,3] átredeződés termikusan megengedett



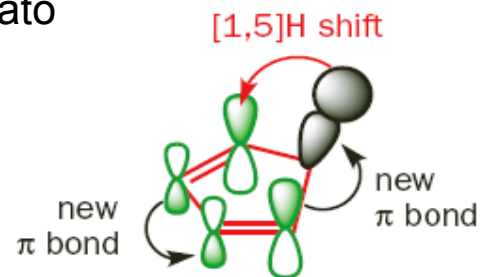
## **[1,5] szigmatróp átrendeződés**



# **Értelmezés a frontális molekulapálya modell alapján**



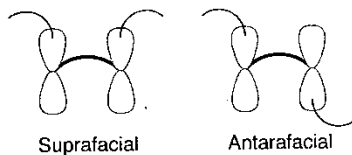
a HOMO is használható



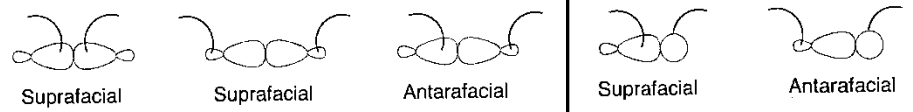


# Értelmezés a Woodward-Hoffmann modell alapján

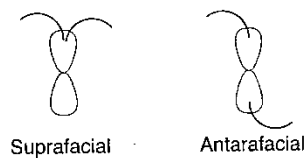
## A. $\pi$ Systems



## B. $\sigma$ Systems

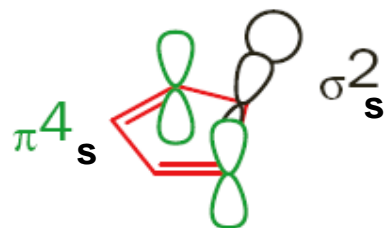


## C. Lone pairs ( $\omega$ )

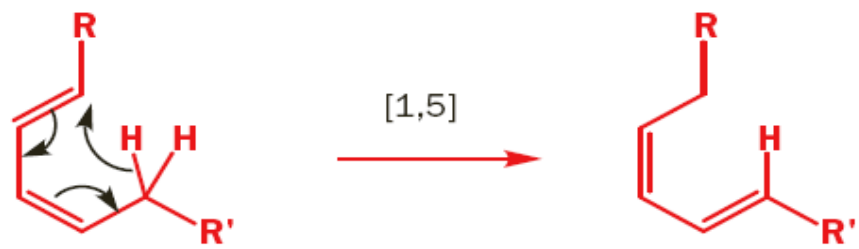


● **Woodward–Hoffmann rules**

In a thermal pericyclic reaction the total number of  $(4q + 2)_s$  and  $(4r)_a$  components must be odd.

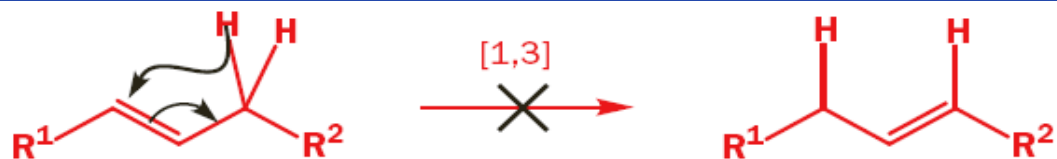


**az [1,5] átrendeződés termikusan megengedett**

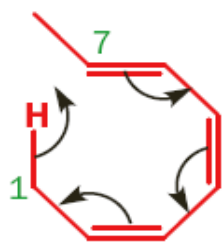


Szuprafaciális hidrogénvándorlás: vándorlás a molekula (gyűrű) egyik felén

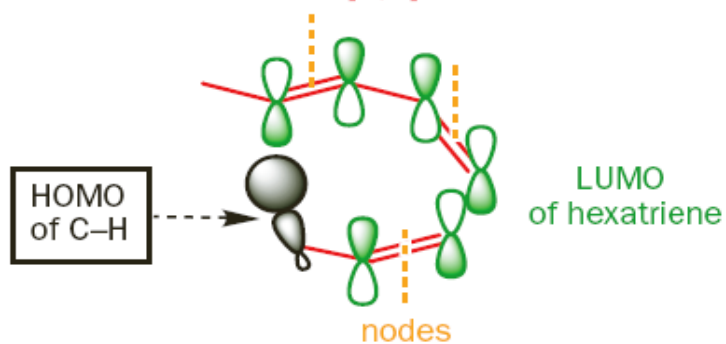
Antarafaciális hidrogénvándorlás: vándorlás közben a hidrogén átmegy a molekula (gyűrű) egyik feléről a másikra



[1,7]H shift

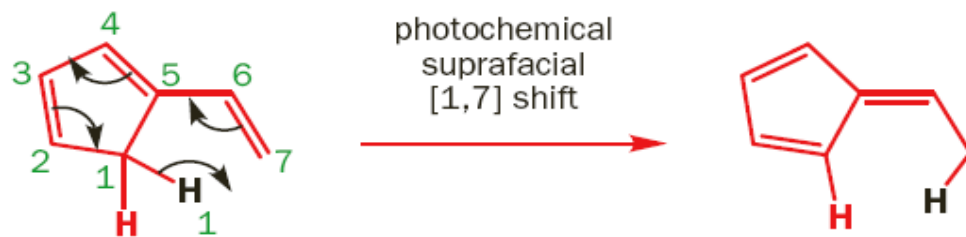


antarafacial [1,7]H shift



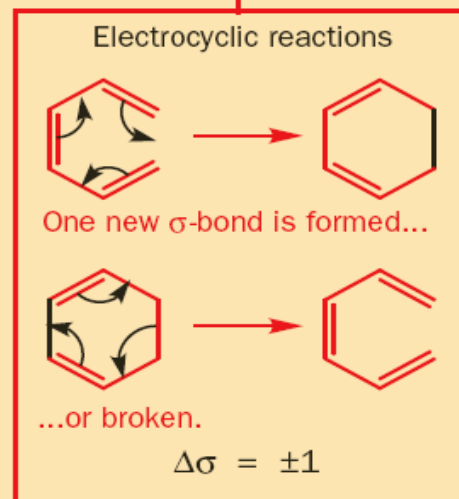
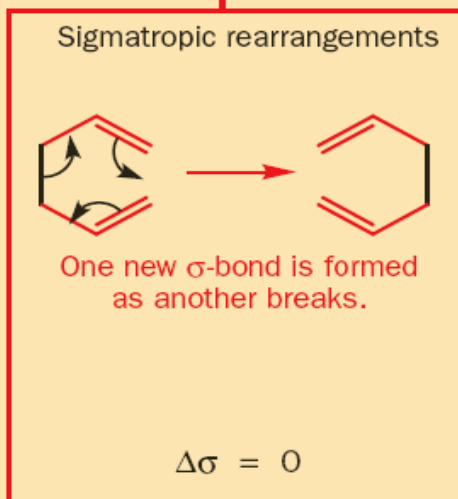
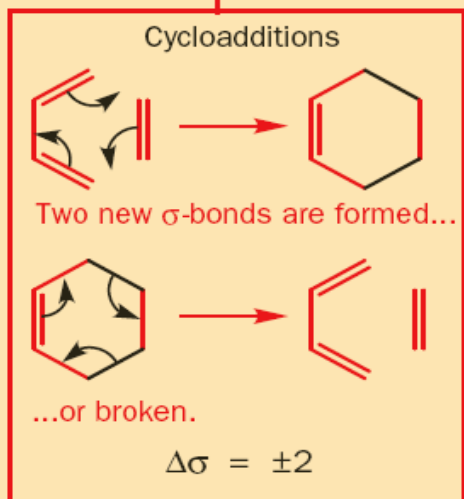
### Summary of thermal sigmatropic hydrogen shifts

	[1,3]H shift	[1,5]H shift	[1,7]H shift
stereochemistry	antarafacial	suprafacial	antarafacial
feasibility	impossible	easy	possible



- The types of pericyclic reactions are distinguished by the number of  $\sigma$  bonds made or broken

Types of pericyclic reactions



# KÖSZÖNÖM A FIGYELMET!

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