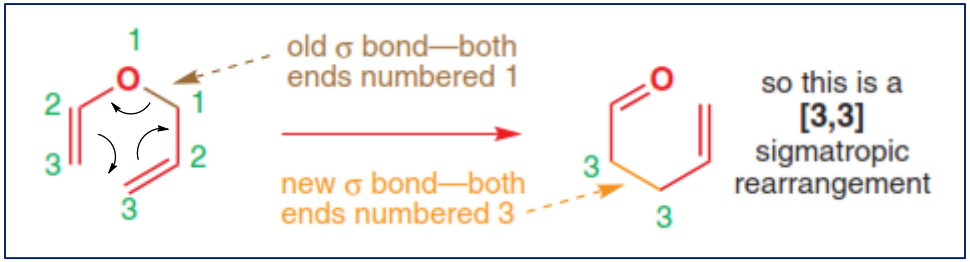
# CYI101
# Common CHEMISTRY(Organic)

**Stereochemistry:** **Pericyclic reactions:** Sigmatropic Rearrangement

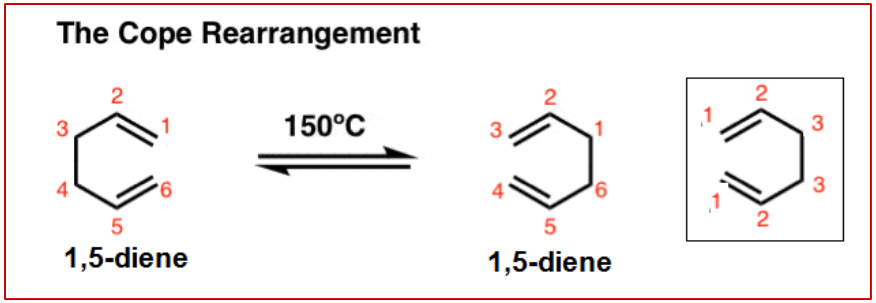
# Sigmatropic Rearrangement: *[3,3] σ*

**Sigmatropic** is a pericyclic reaction wherein a *σ bond* appears to move from one place to another during the reaction.

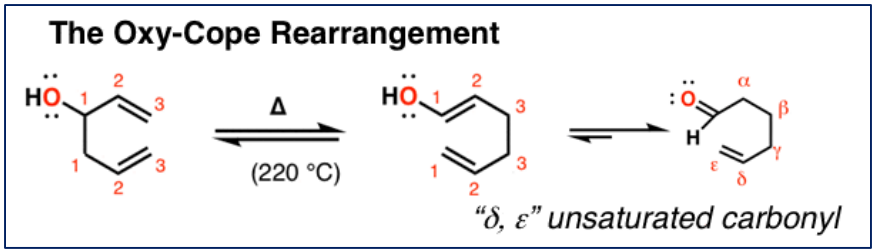
[3,3] Claisen Rearrangement



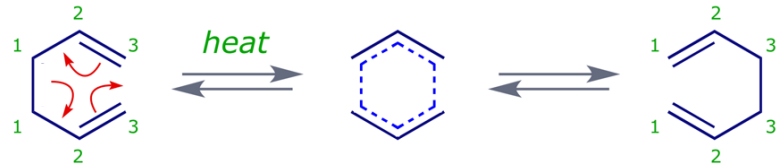

[3,3] Cope Rearrangement

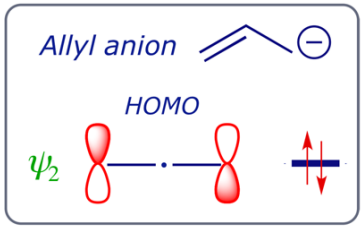



[3,3] Oxy-cope Rearrangement



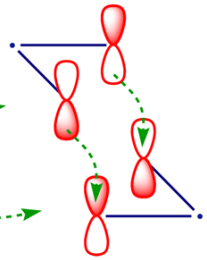
# Sigmatropic Reactions: *[3,3] Cope Rearrangement*




LUMO (2e⁻)
allyl cation $\psi_2$

HOMO (4e⁻)
allyl anion $\psi_2$



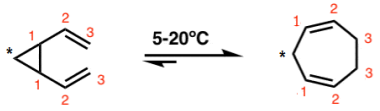
*[3,3] Sigmatropic rearrangement viewed as the **[π4s + π2s] cycloaddition** of allyl anion to allyl cation. Both components can react **suprafacially** through a chair-like transition structure.*

**The Cope Rearrangement Equilibrium Will Favor The More Substituted Alkene**

15 : 85

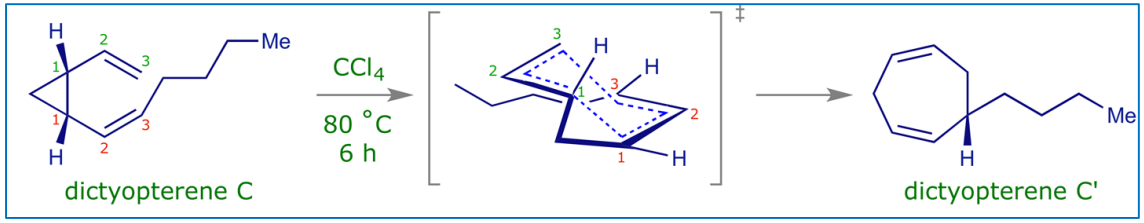
Monosubstituted alkene — Disubstituted alkene (more stable)

**A Room-Temperature Cope Rearrangement That Relieves Ring Strain**



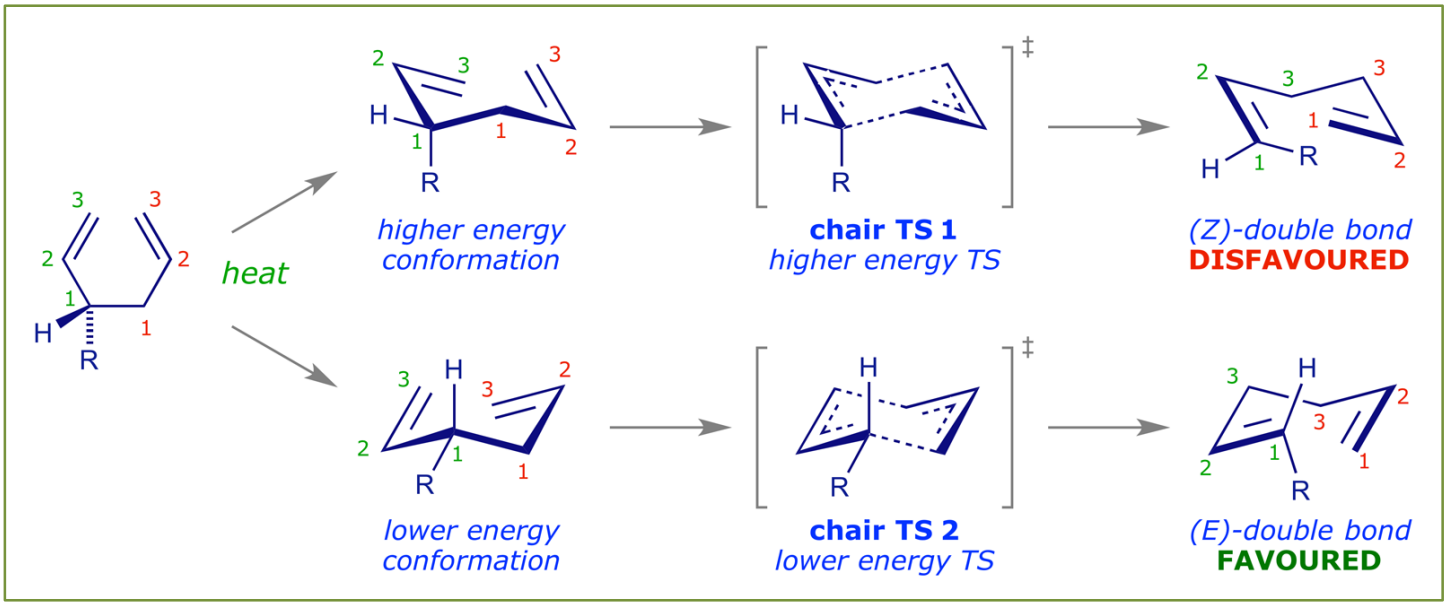

*Cyclopropane ring strain: about 27 kcal/col*

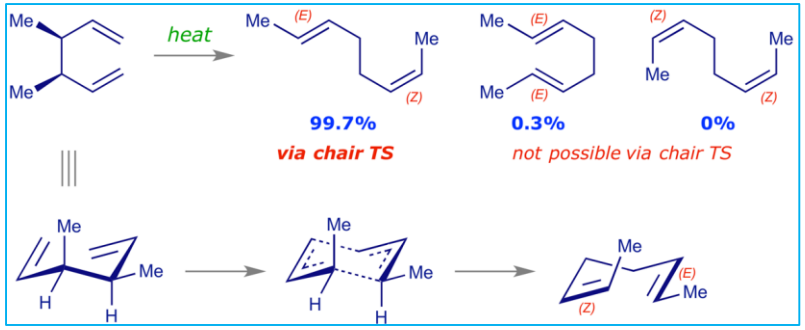
*only product*

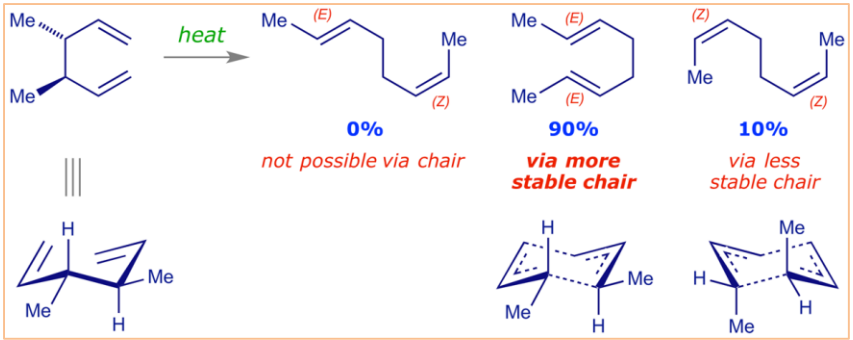



dictyopterene C — dictyopterene C'

# [3,3] Cope Rearrangement: *Stereochemical Preference*

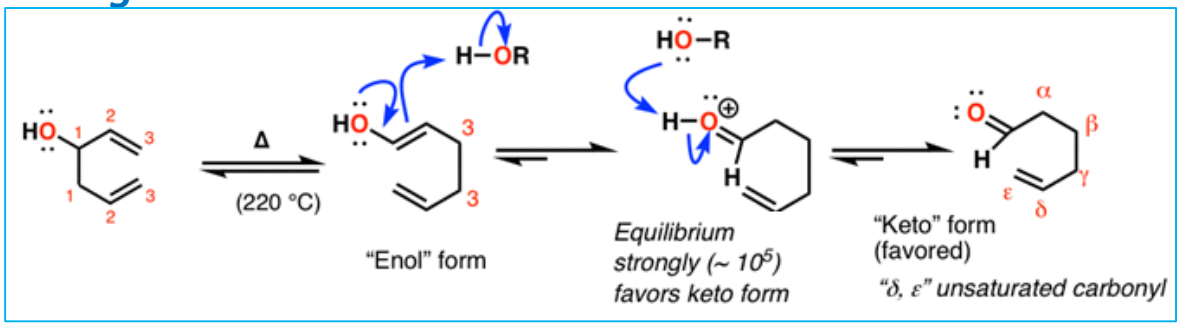


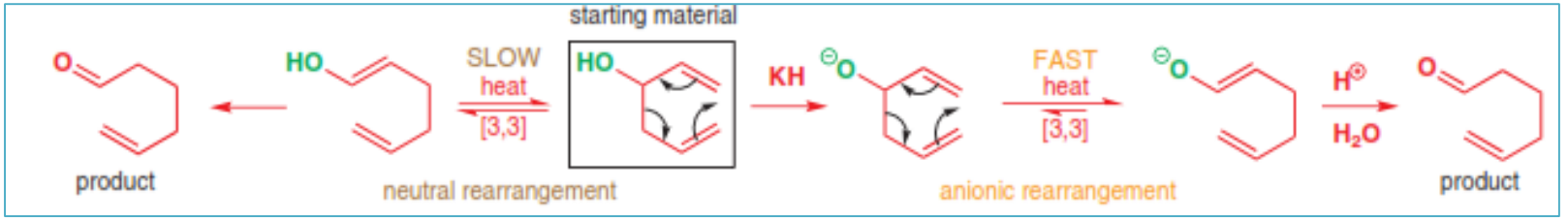



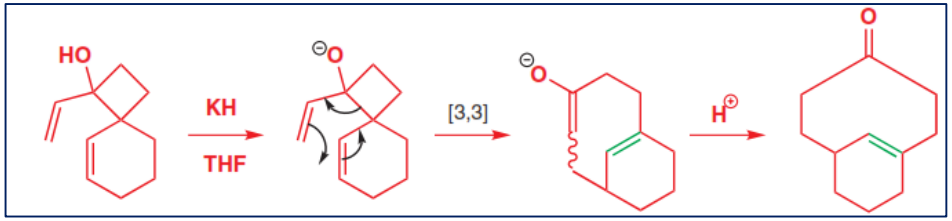



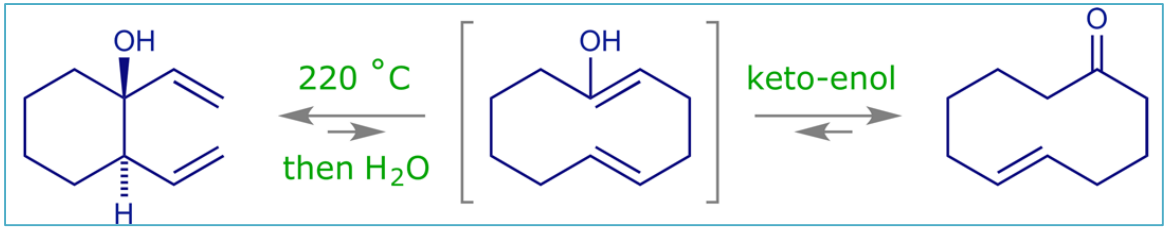
# Sigmatropic Reactions: *[3,3] Oxy-Cope Rearrangement*

## *Oxy-Cope Rearrangement*

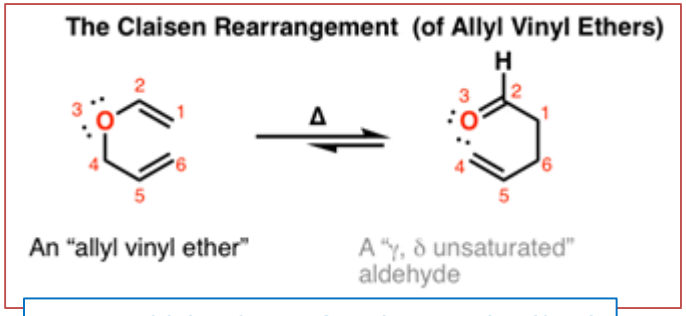


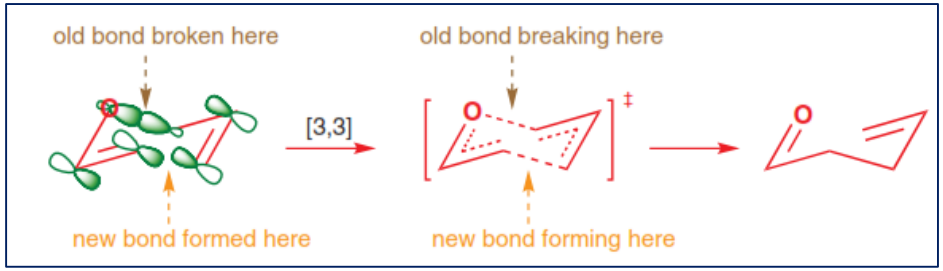



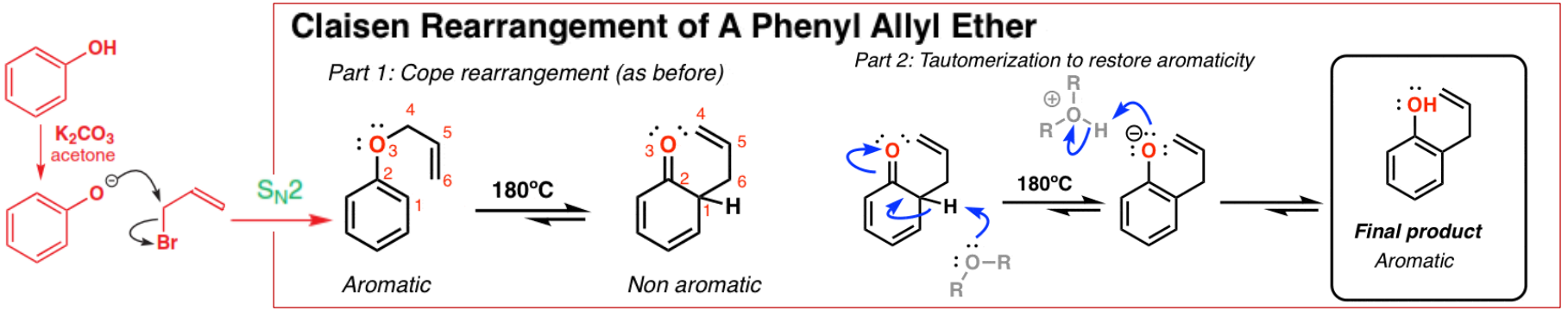



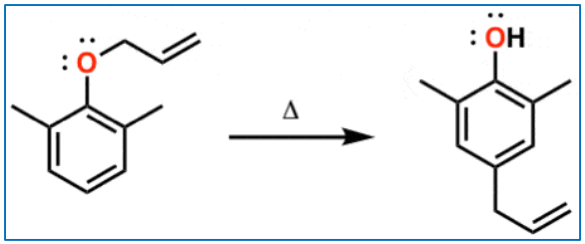
# Sigmatropic Reactions: *[3,3] Claisen Rearrangement*

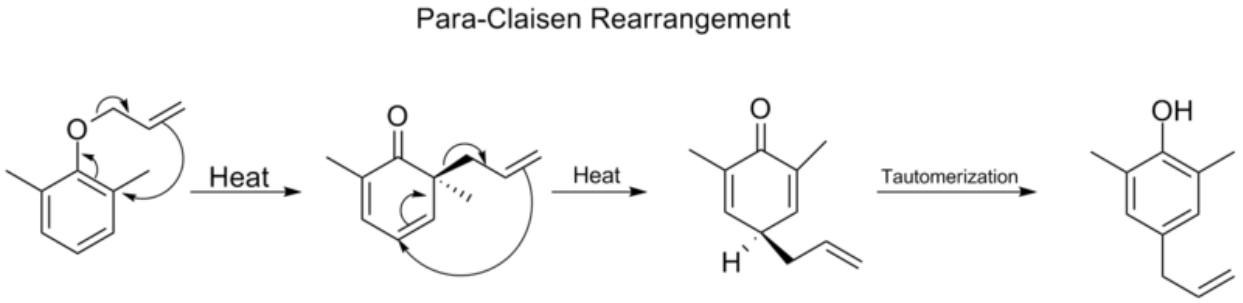



*Strong driving force: ΔH about 20 kcal/mol (replace C-C pi bond with C-O pi bond)*

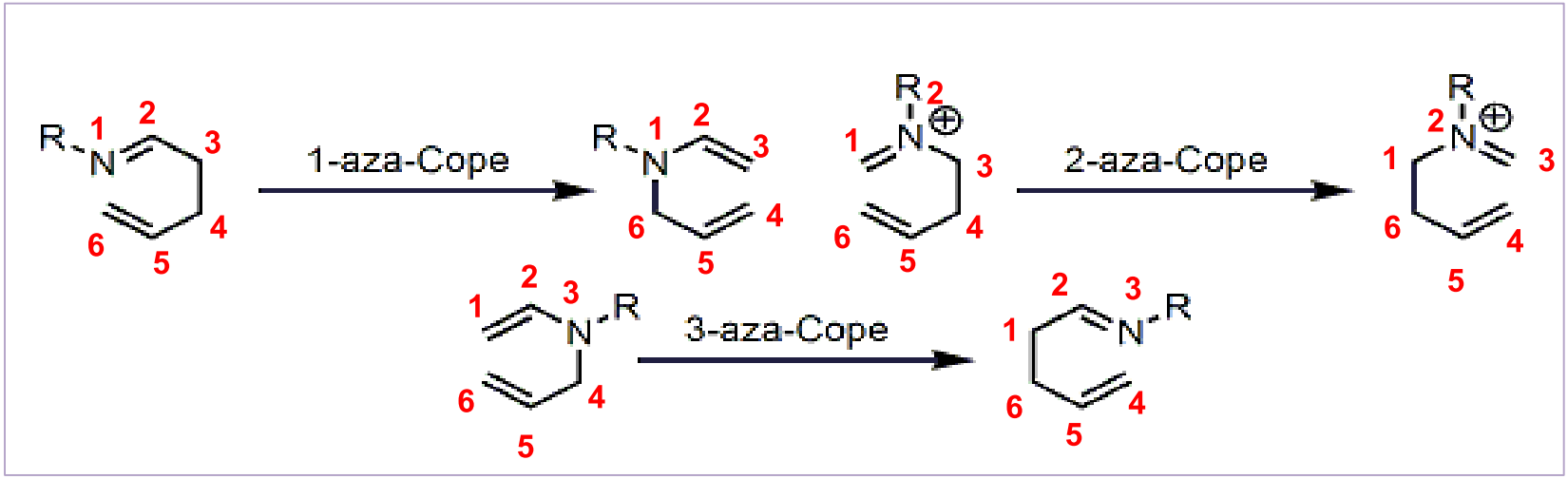


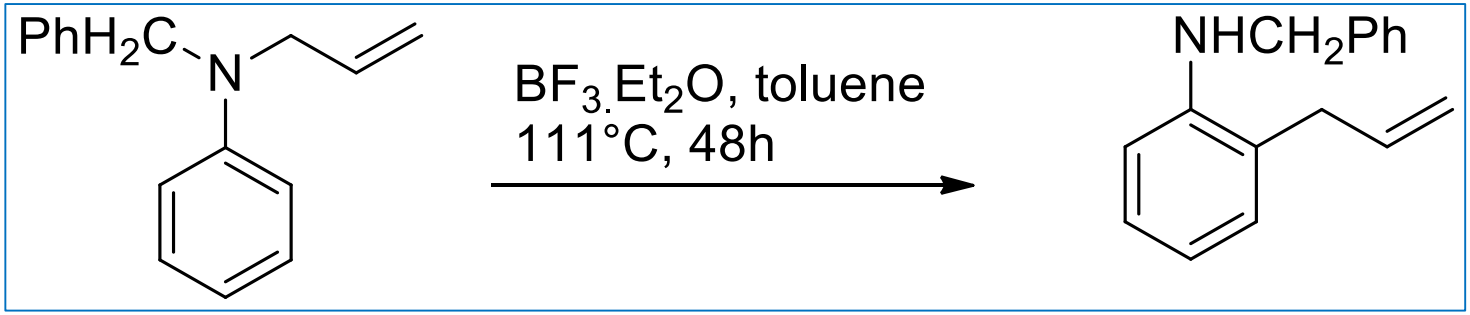



# [3,3] Rearrangement: *Aza-Cope and Aza-Claisen*

## Aza-Cope Rearrangement

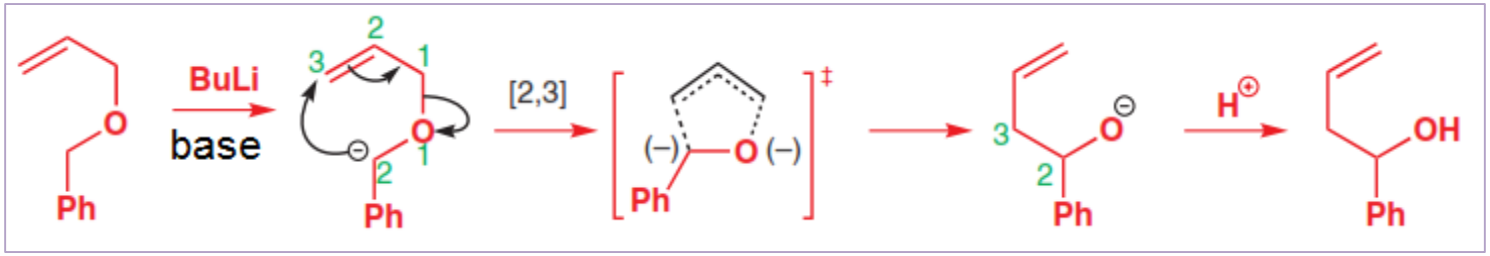



## Aza-Claisen Rearrangement

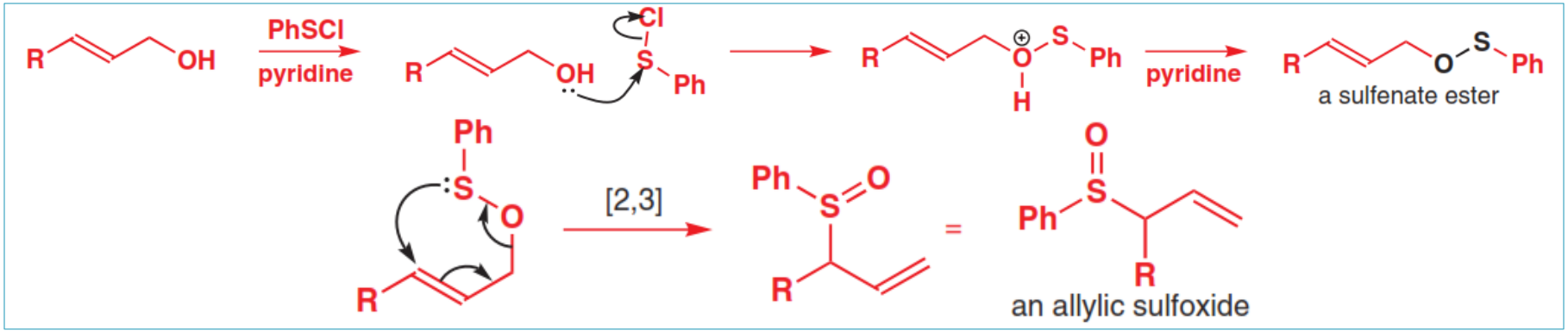


# Pericyclic Reactions: *[2,3] Sigmatropic Rearrangement*

## [2,3]-Sigmatropic rearrangements

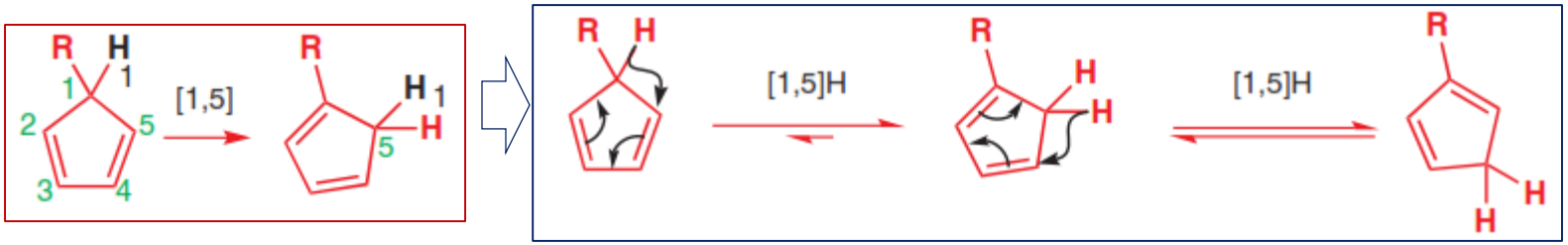



## [2,3]-Sigmatropic rearrangements with S

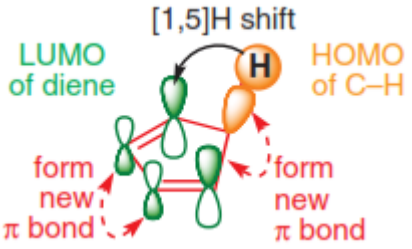


# Pericyclic Reactions: *[1,n] H Sigmatropic Shift*

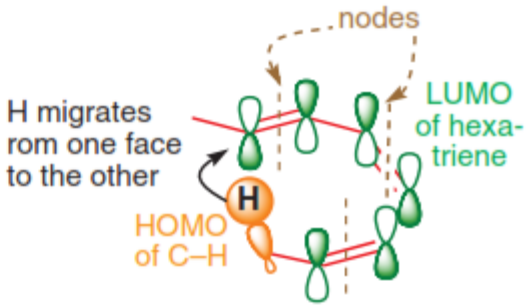
## [1,5]-Sigmatropic hydrogen shifts



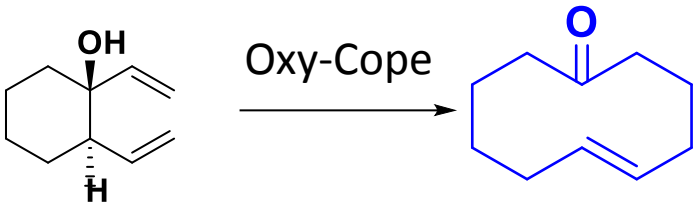

## Orbital description for the [1,5]H sigmatropic shift

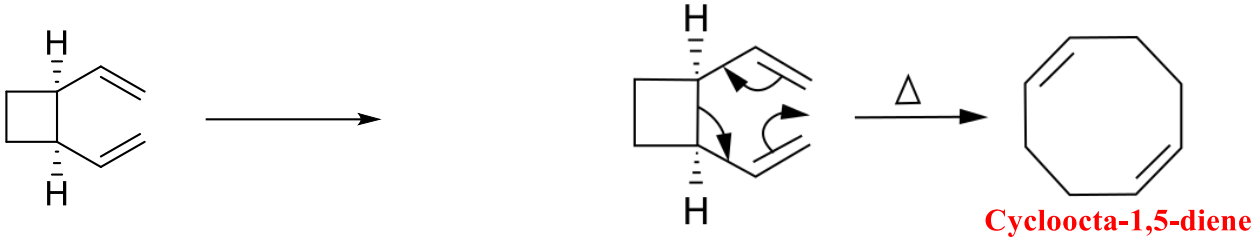



allowed and possible antarafacial [1,7]H shift

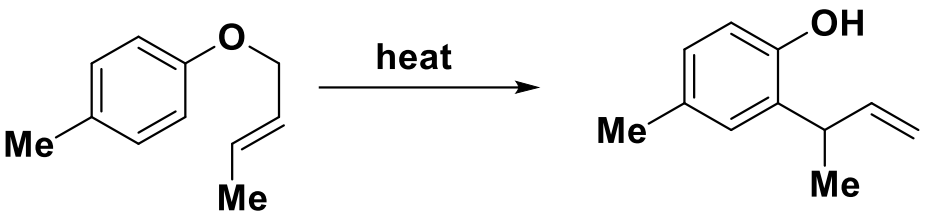



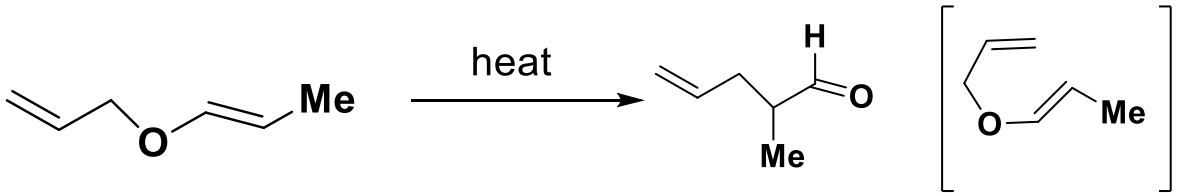
# Chemistry Problem



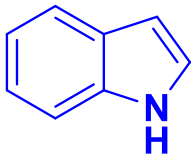




Cycloocta-1,5-diene

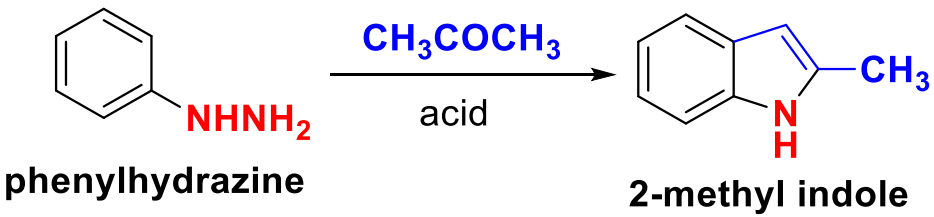


# [3,3] Sigmatropic Rearrangement : Fischer Indole Synthesis



Indole

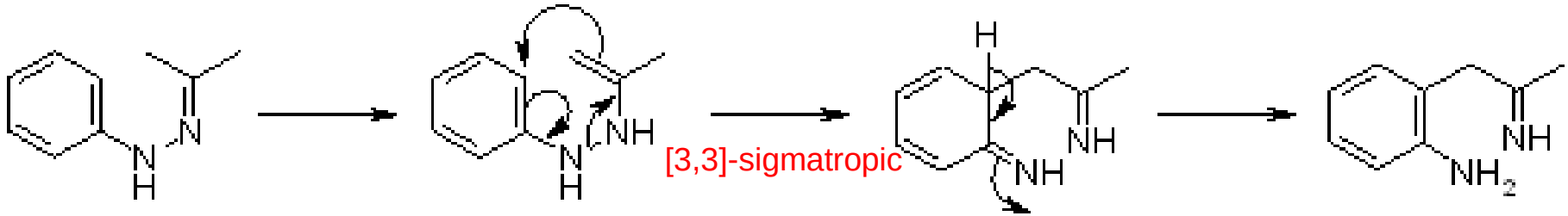


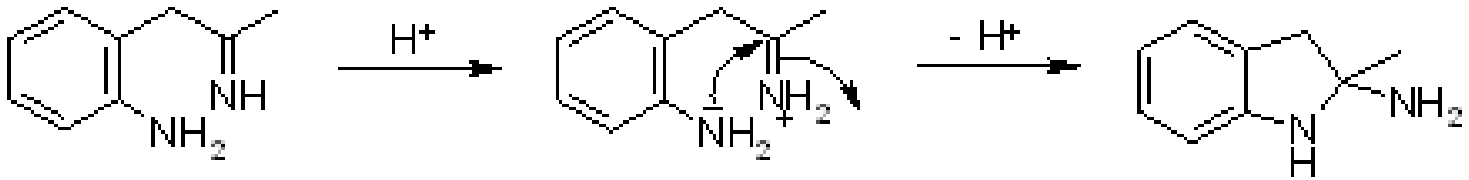

phenylhydrazine

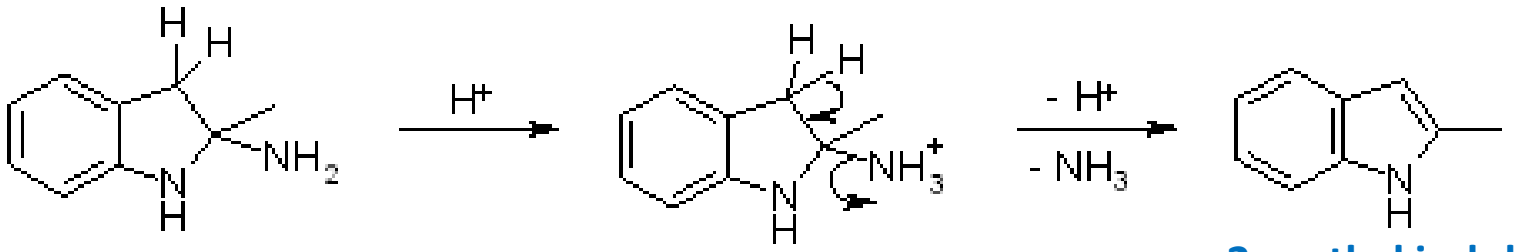
2-methyl indole

The conversion of aryl hydrazones to indoles; requires elevated temperatures and the addition of Brønsted or Lewis acids.

## Mechanism



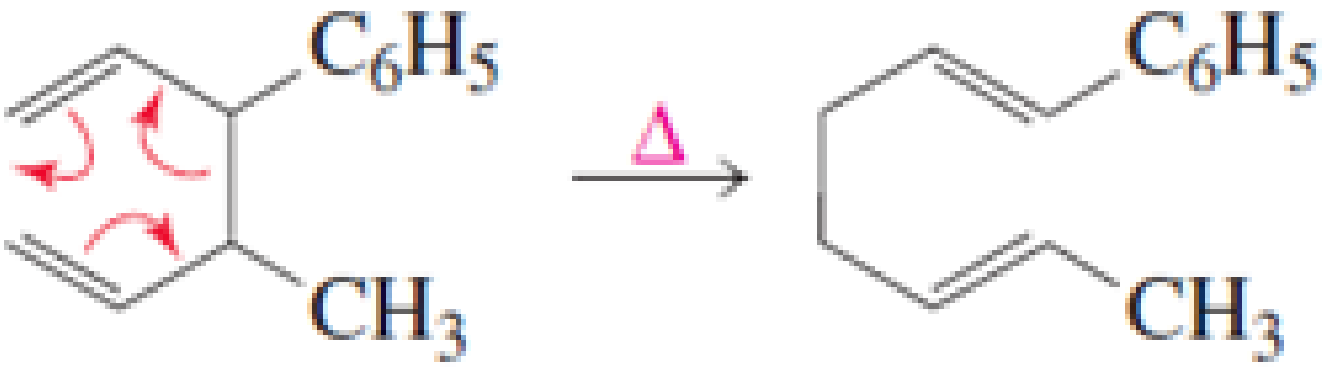




2-methyl indole

# [3,3] Sigmatropic Rearrangement

## a Cope rearrangement




## a Claisen rearrangement