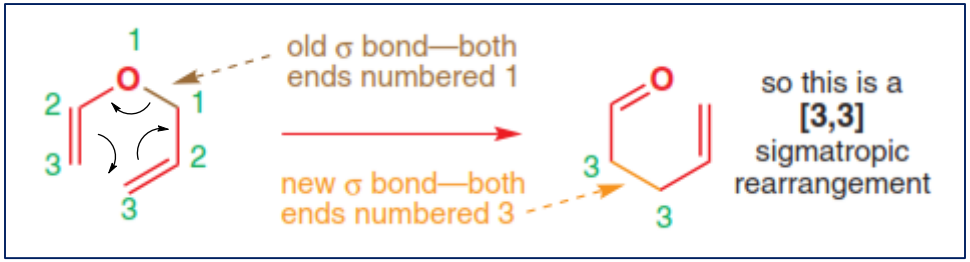
CYI101
Common CHEMISTRY(Organic)

Stereochemistry: **Pericyclic reactions:** Sigmatropic Rearrangement

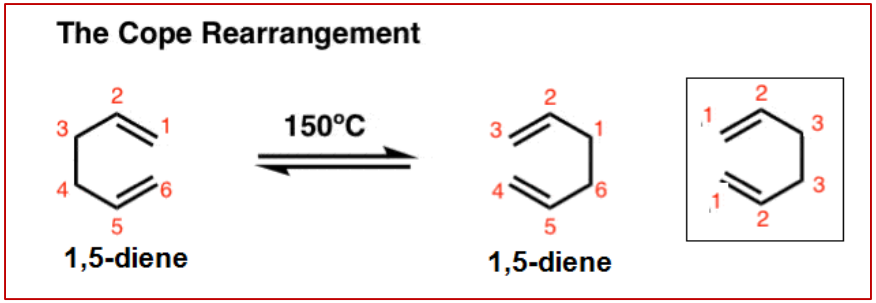
Sigmatropic Rearrangement: *[3,3] σ*

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

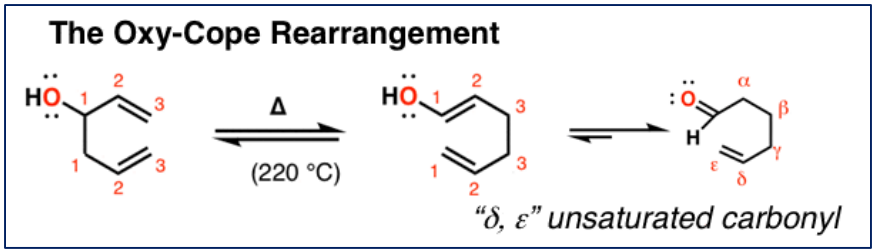
[3,3] Claisen Rearrangement



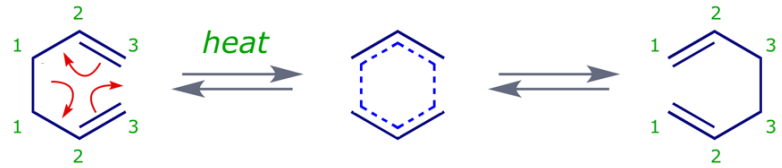
[3,3] Cope Rearrangement

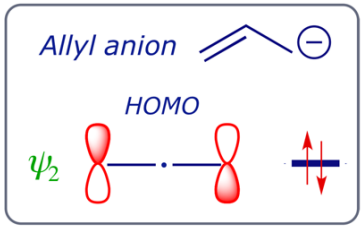


[3,3] Oxy-cope Rearrangement



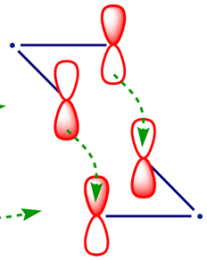
Sigmatropic Reactions: *[3,3] Cope Rearrangement*





LUMO (2e⁻)
allyl cation ψ_2

HOMO (4e⁻)
allyl anion ψ_2



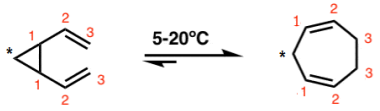
*[3,3] Sigmatropic rearrangement viewed as the **[π4s + π2s] cycloaddition** of allyl anion to allyl cation. Both components can react **suprafacially** through a chair-like transition structure.*

The Cope Rearrangement Equilibrium Will Favor The More Substituted Alkene

15 : 85

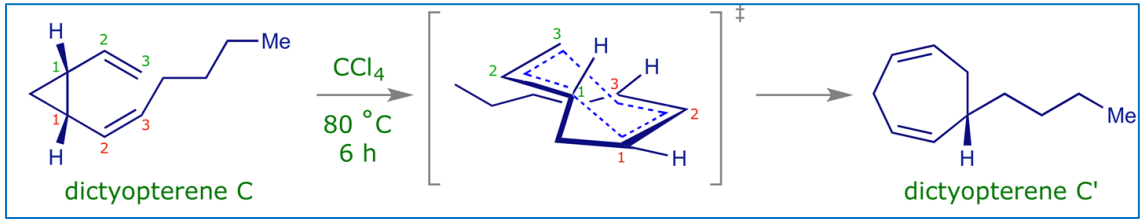
Monosubstituted alkene — Disubstituted alkene (more stable)

A Room-Temperature Cope Rearrangement That Relieves Ring Strain



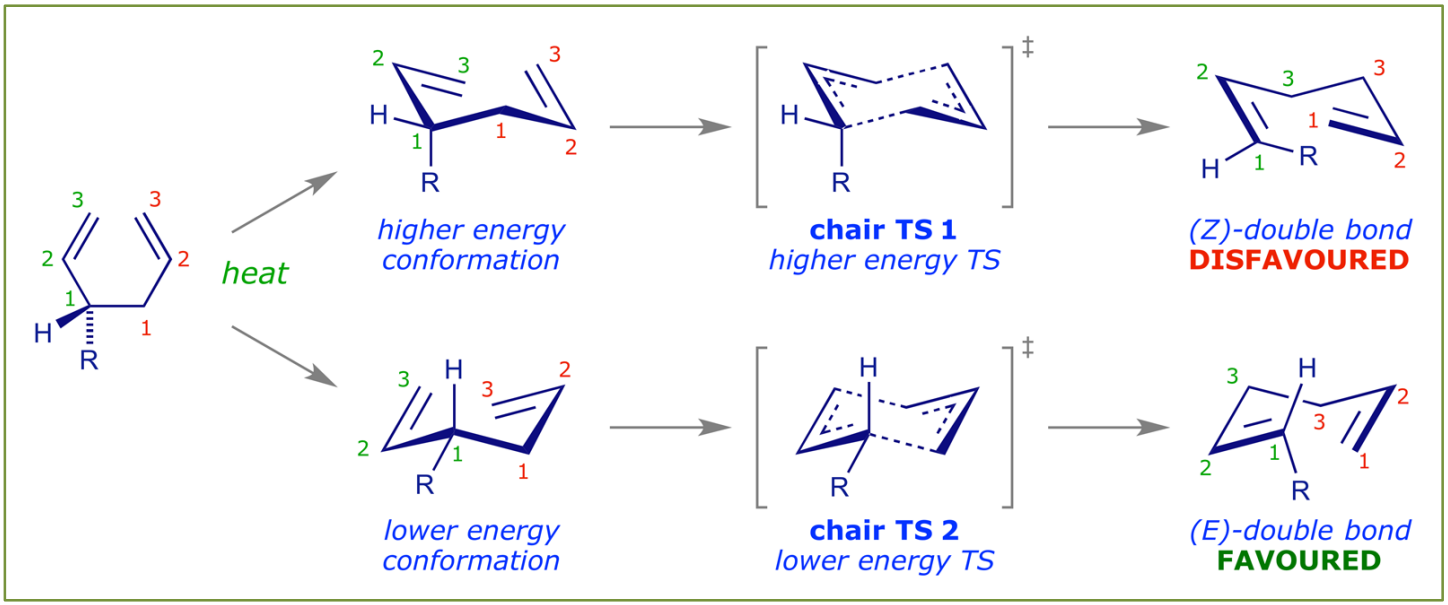
Cyclopropane ring strain: about 27 kcal/col

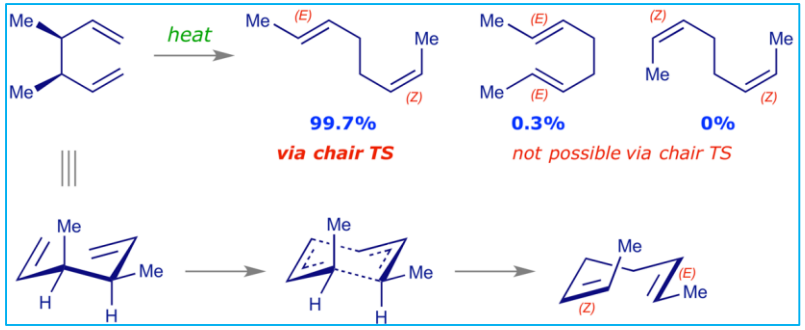
only product

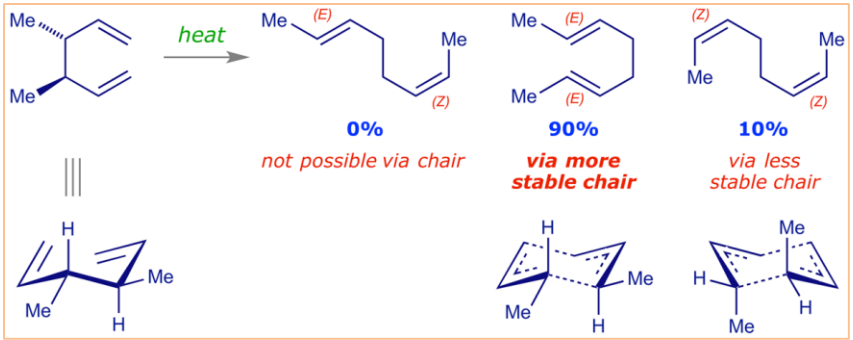


dictyopterene C — dictyopterene C'

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

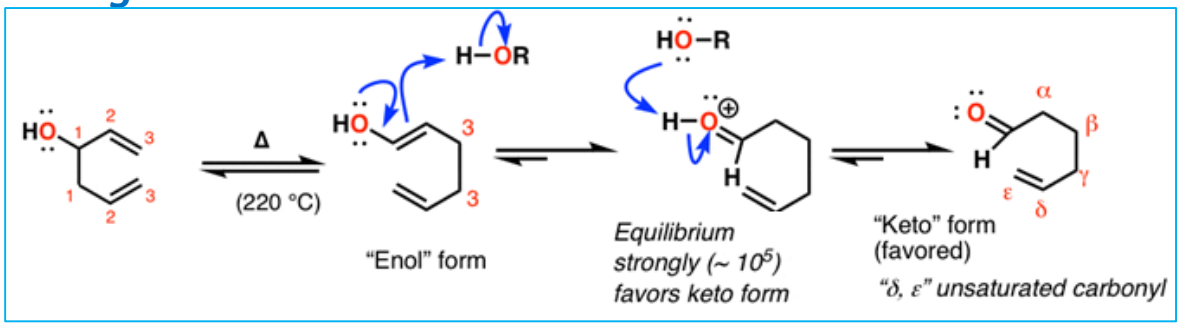


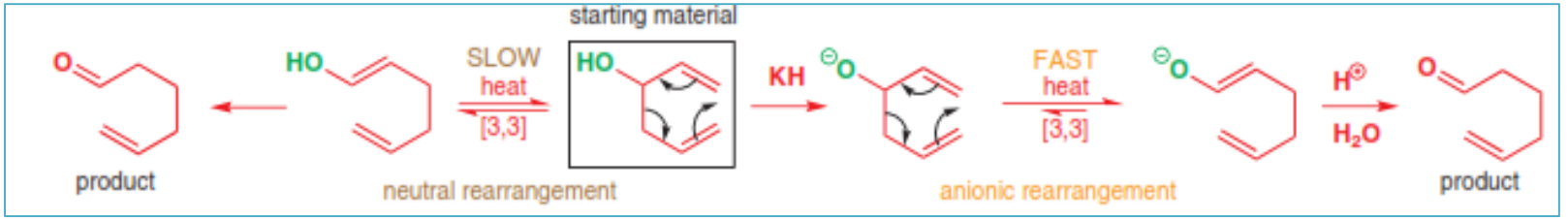


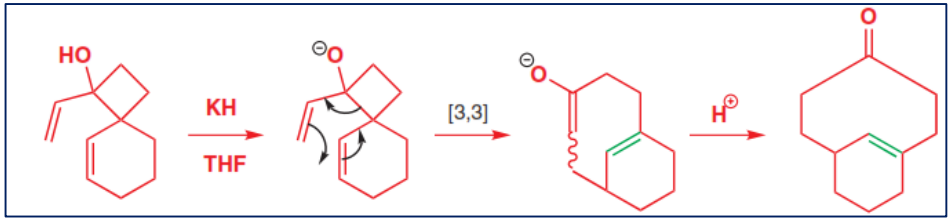


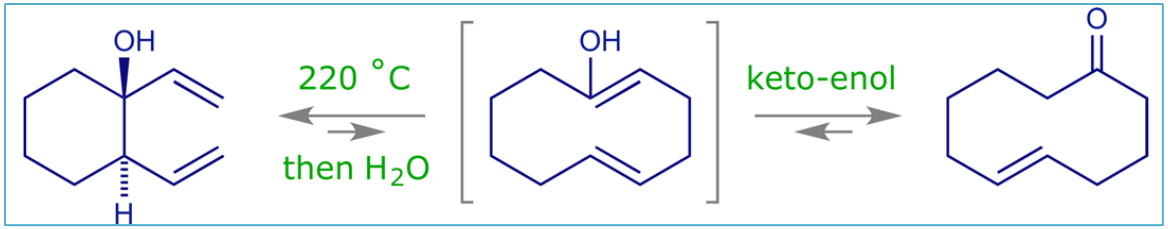
Sigmatropic Reactions: *[3,3] Oxy-Cope Rearrangement*

Oxy-Cope Rearrangement

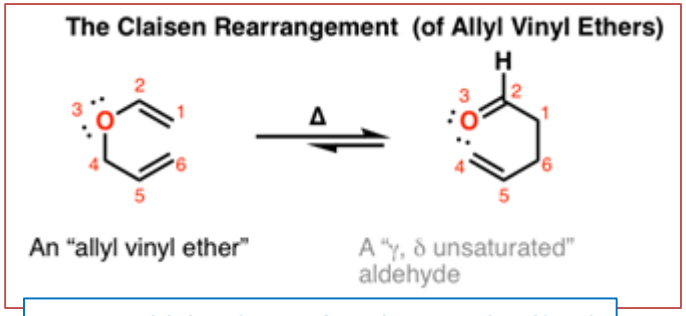


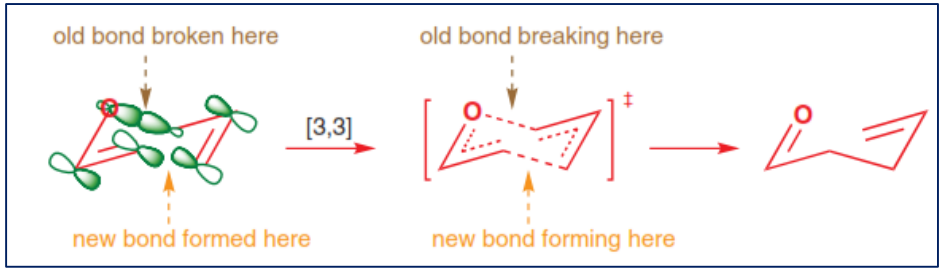




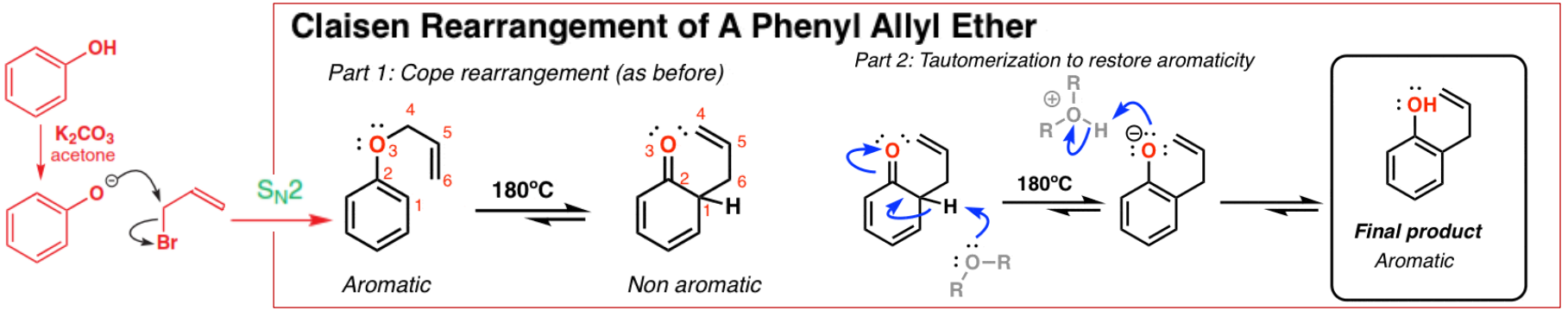


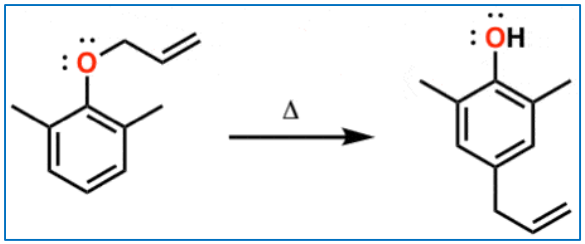
Sigmatropic Reactions: *[3,3] Claisen Rearrangement*

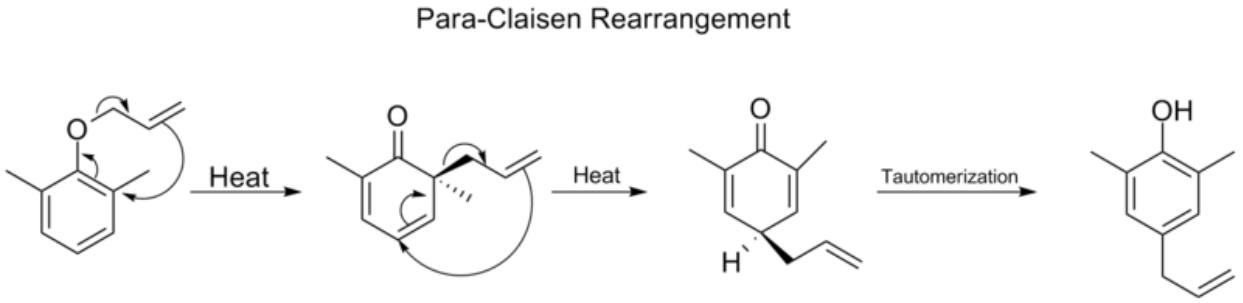




Strong driving force: ΔH about 20 kcal/mol (replace C-C pi bond with C-O pi bond)

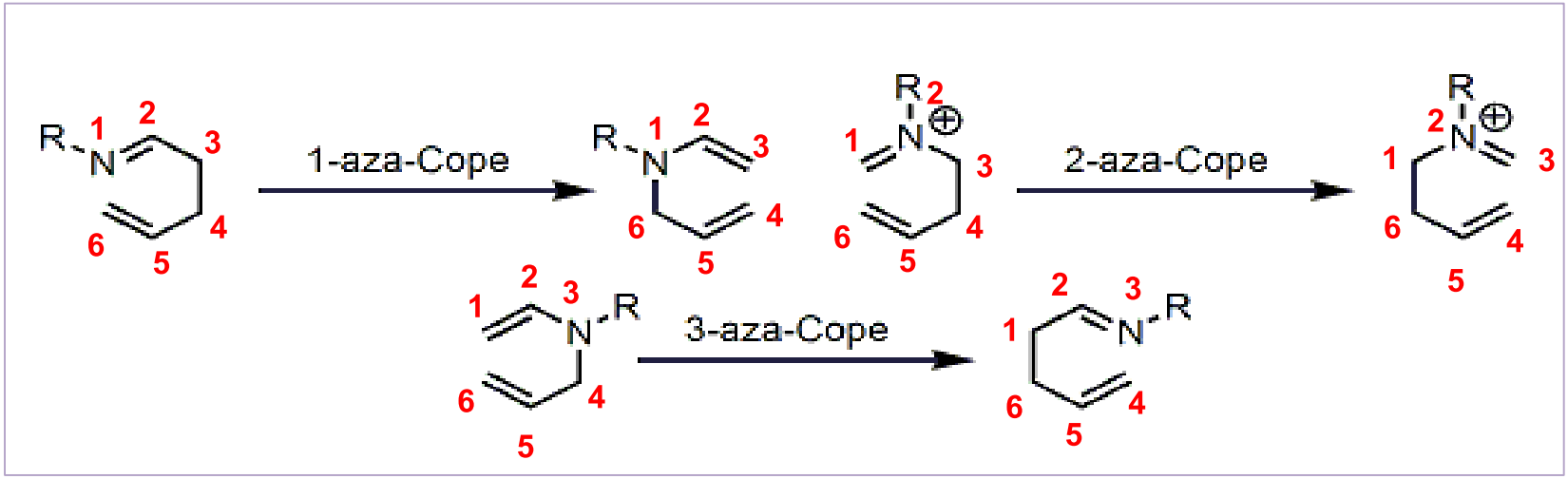




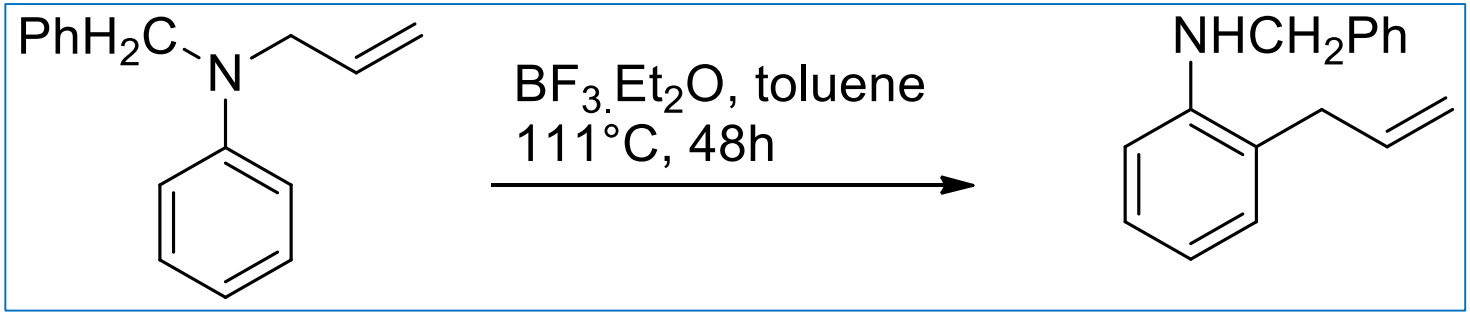


[3,3] Rearrangement: *Aza-Cope and Aza-Claisen*

Aza-Cope Rearrangement

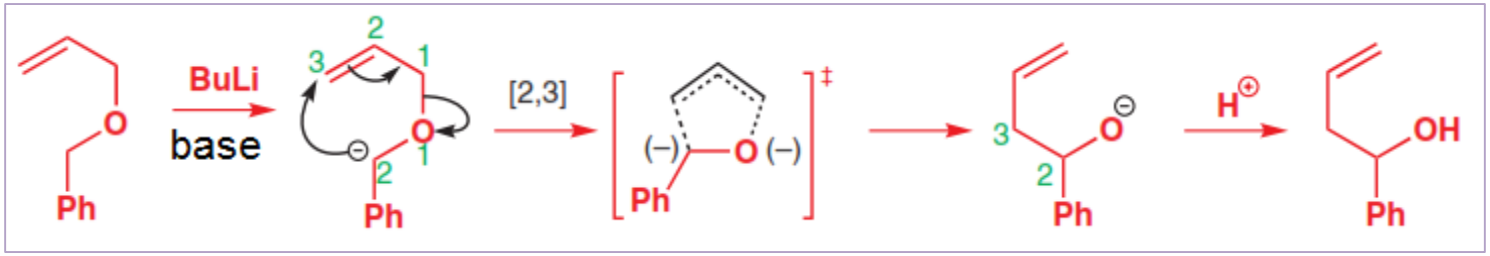


Aza-Claisen Rearrangement

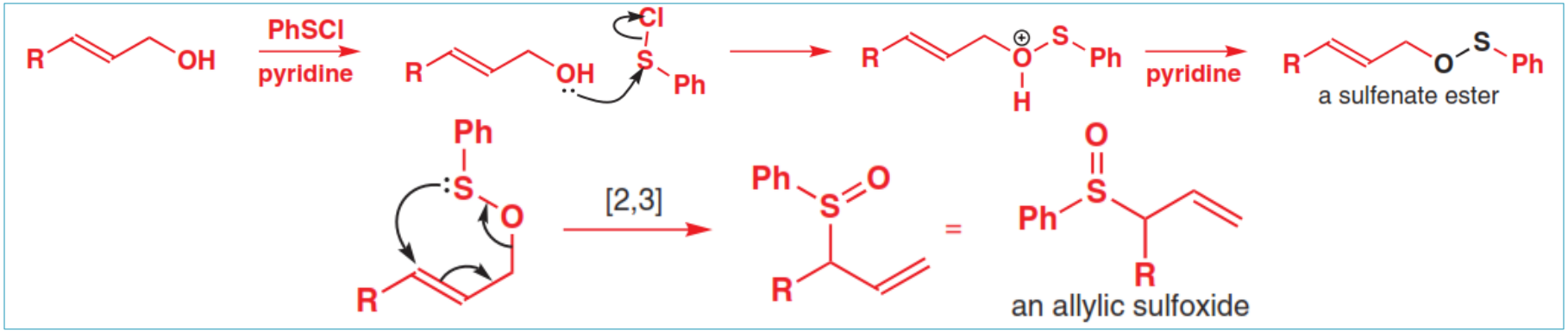


Pericyclic Reactions: *[2,3] Sigmatropic Rearrangement*

[2,3]-Sigmatropic rearrangements

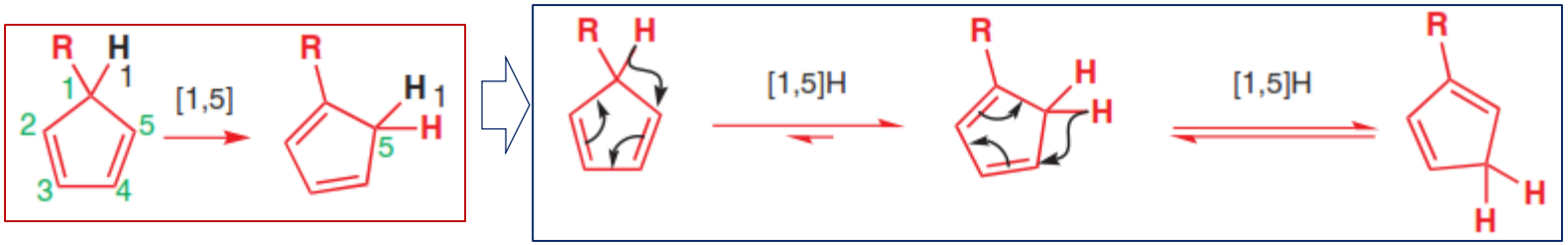


[2,3]-Sigmatropic rearrangements with S

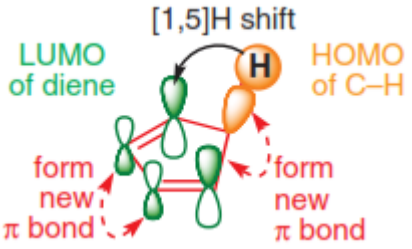


Pericyclic Reactions: *[1,n] H Sigmatropic Shift*

[1,5]-Sigmatropic hydrogen shifts



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



allowed and possible antarafacial [1,7]H shift