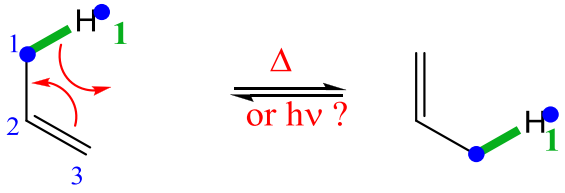
Overheads: - Today's Outline

Recap Sigmatropic Reactions:

WH Rule:	4n / even	Δ	= antara X
		hν	= supra
	4n+2 / odd	Δ	= supra
		hν	= antara X

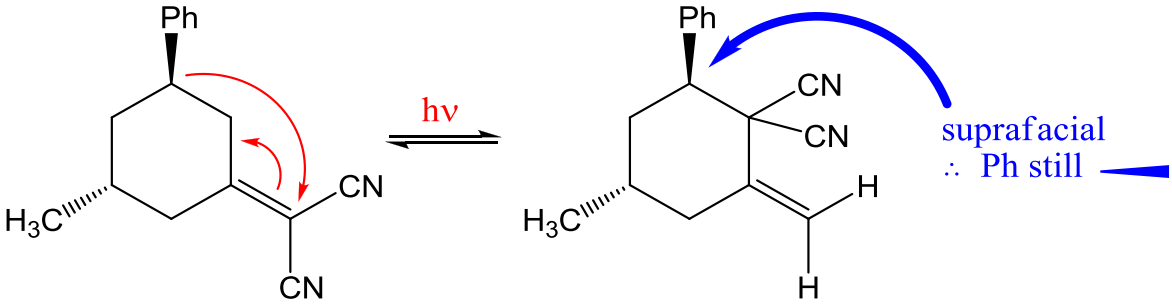
***identical rule as for cycloaddition!

Example: [1,3] rearrangement



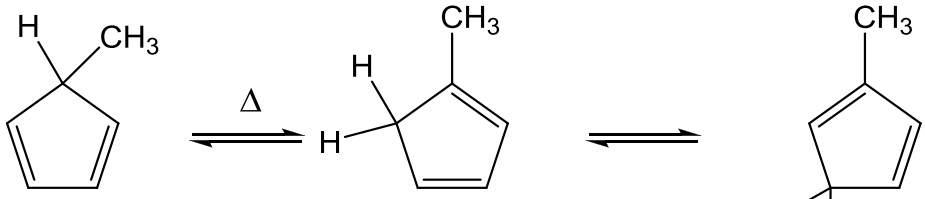
even ∴ hν

e.g.



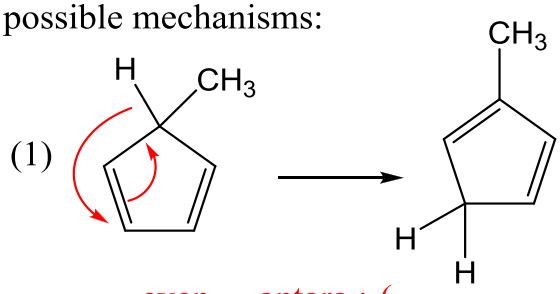
More common examples are thermal/odd pairs. 6 e⁻ most common: [3,3] or [1,5]

e.g.

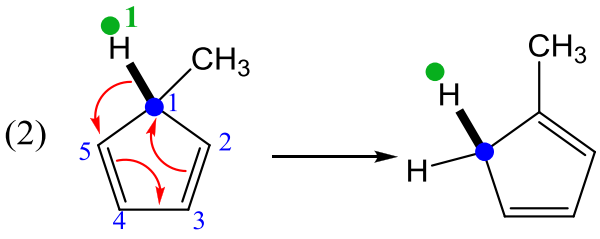


methylcyclopentadiene (aka Cp')
- CH_3 "jumps" between all 5 carbons)

2 possible mechanisms:



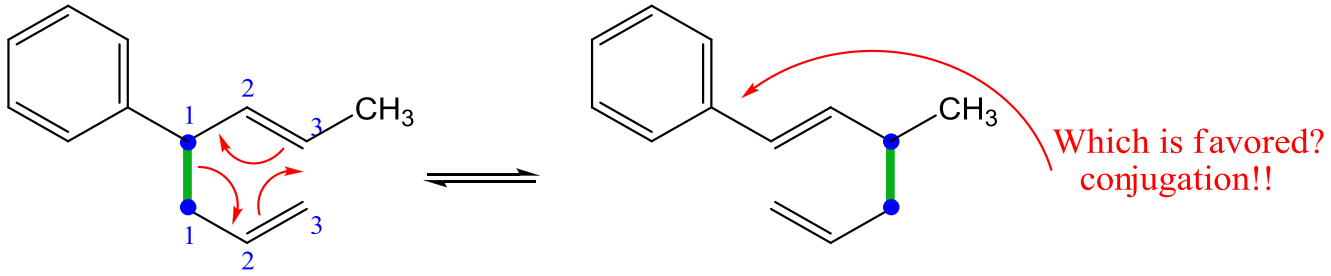
even ∴ antara :-(



odd ∴ supra :-)
[1,5]=sigmatropic

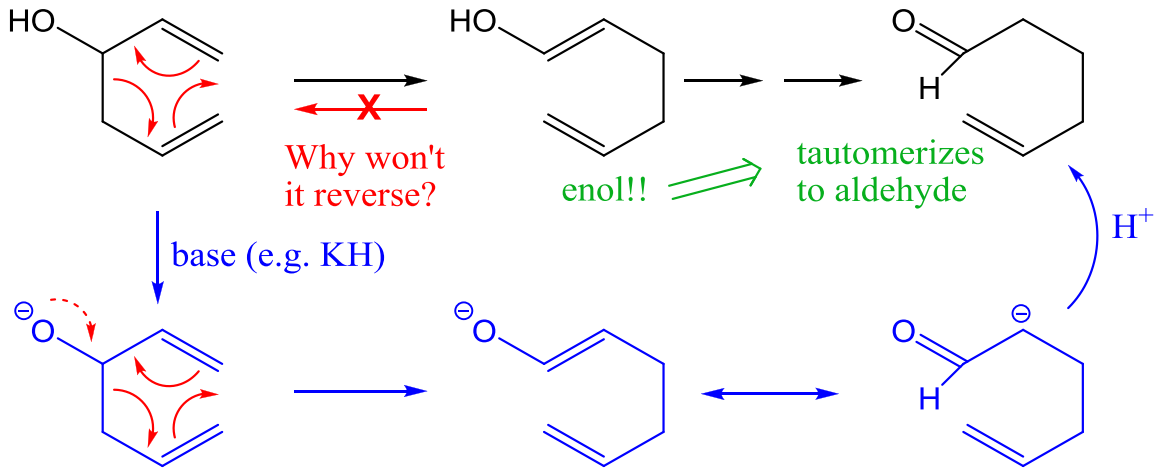
Some Common [3,3] rearrangements:

(A) Cope Rearrangement



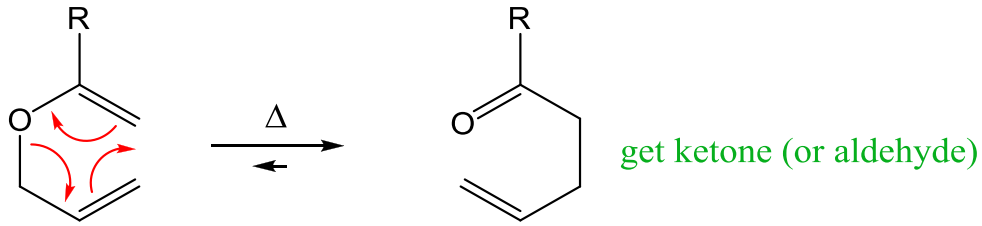
** always look for Cope with 1,5-diene:

(B) Oxy-Cope (with OH substituent)



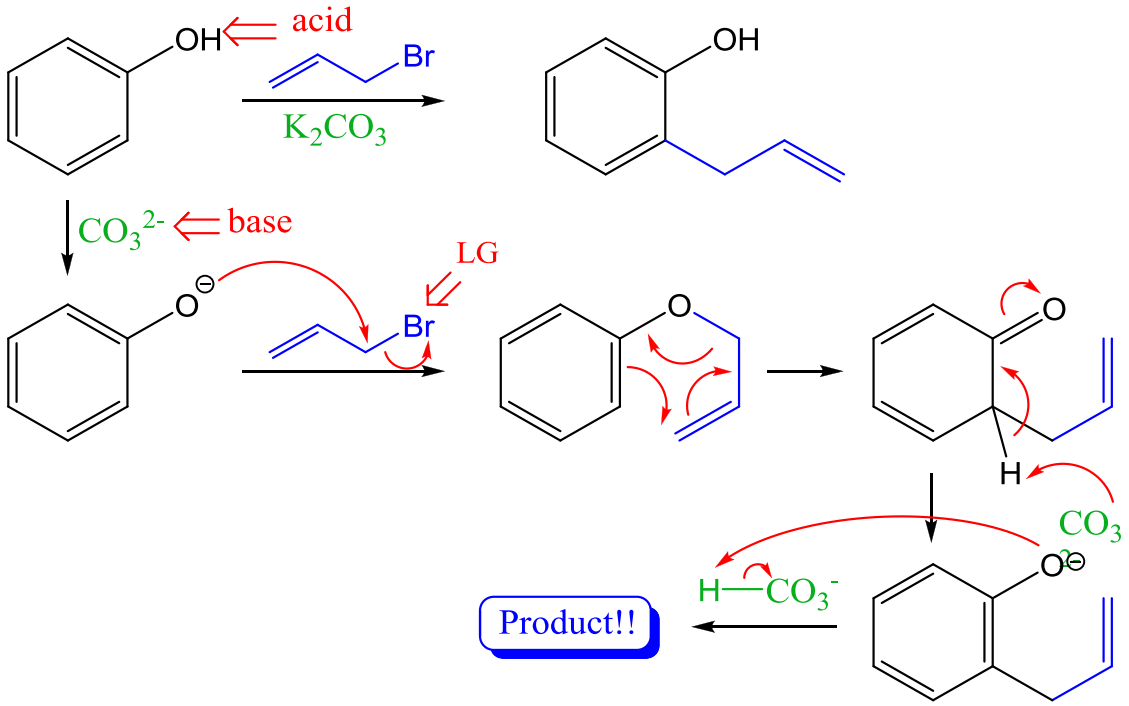
- anionic Oxy-Cope: much faster (10^{12} times!)
  - O^- helps "push" e^- on their way

(C) Claisen Rearrangement (O in chain)

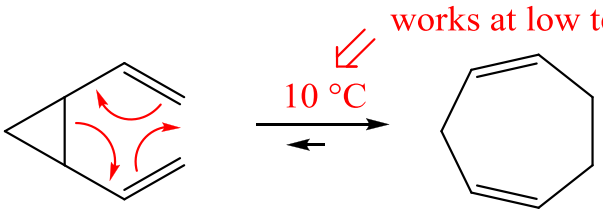


get ketone (or aldehyde)

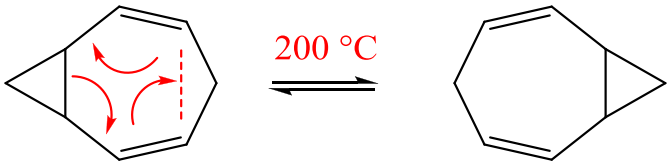
Example: Propose a mechanism for:



Special case:



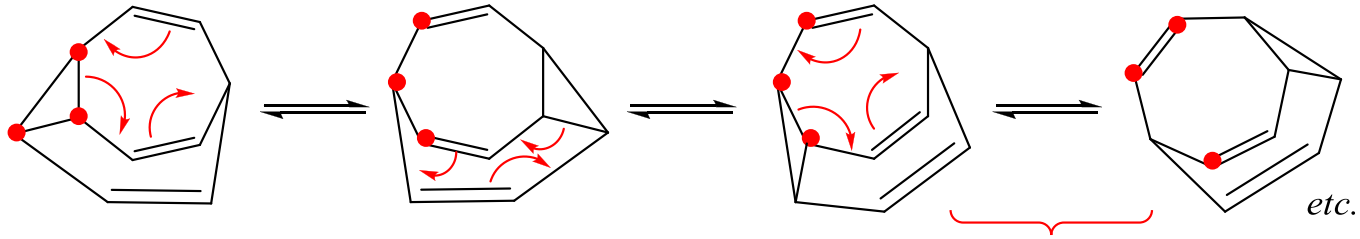
- relieves ring strain, so very easy



- get rapid interconversion at high temp

→ called valence tautomerism: rapid reorganization of bonding electrons.

Very Interesting Molecule:



● C's get scrambled everywhere

→ at 25°C ^{1}H NMR = 2 broad peaks (in 6:4 ratio)

→ at 100°C ^{1}H NMR & ^{13}C NMR: one sharp peak only!

→ reaction is so fast at 100°C that all C's/H's end up in all positions

→ 1.2 million forms (= 10!/3) - all rapidly interconverting at 100°C

⇨ molecule is called Bullvalene

- After William "Bull" Doering (1917-2011)– who imagined/proposed the structure in 1961. Was actually made in 1963, proving Doering's theory