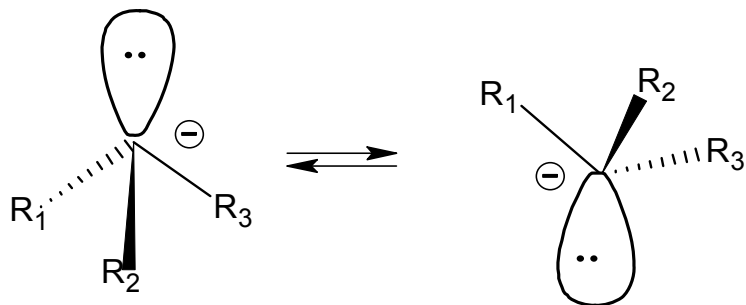


Carbanions

CH_3^- , 8-e structure isoelectronic to NH_3 : must be pyramidal



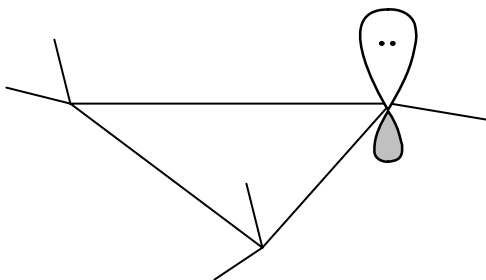
The barrier to inversion is only 1-2 kcal/mol

It is very fast and simple carbanions act as planar

If we would like to stabilize the pyramidal structure, the barrier to inversion should be increased. How?

1. More electronegative substituents

2. Sterically. Put the anion in a small ring



sp^3 - 109.5

Ring- 60°

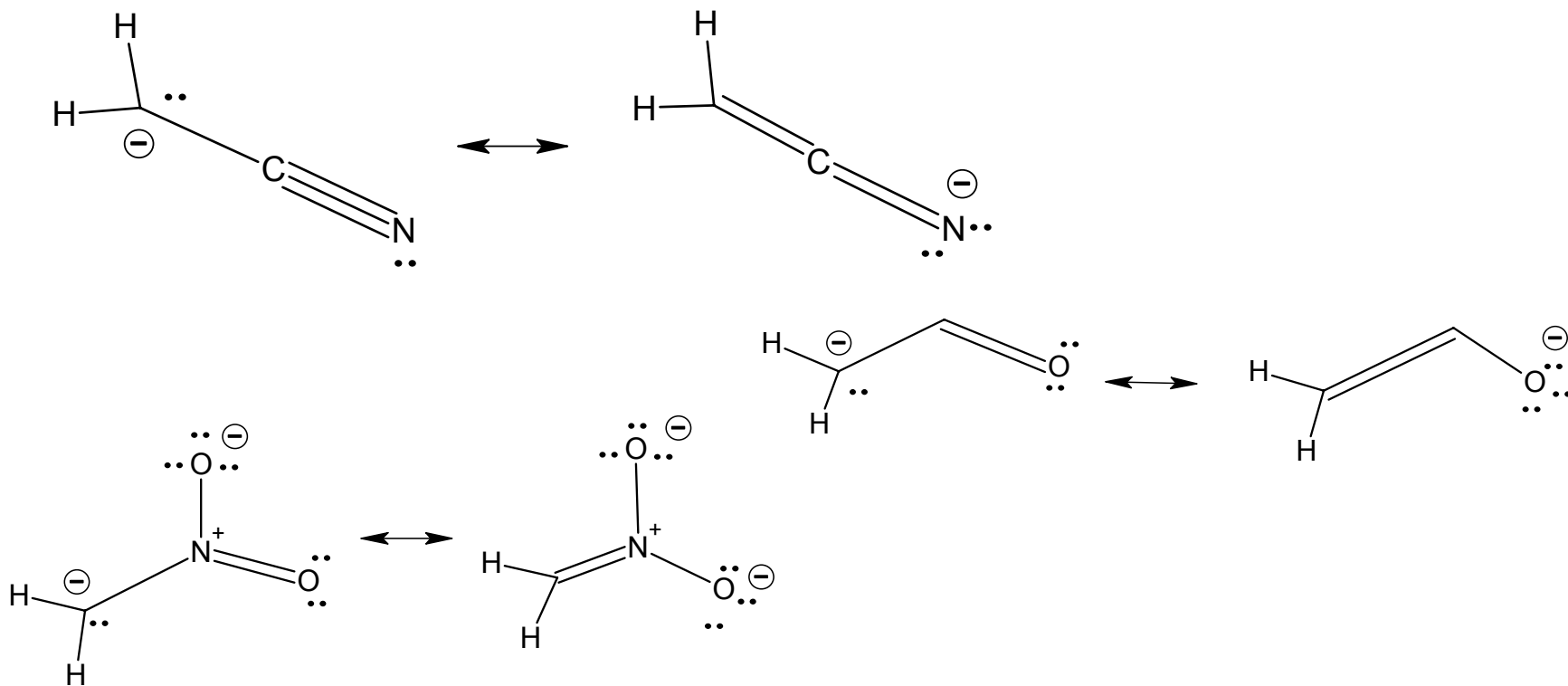
sp^2 - 120.0

sp^3 is closer to the ring angle

Stabilization of planar structure by π -delocalization.

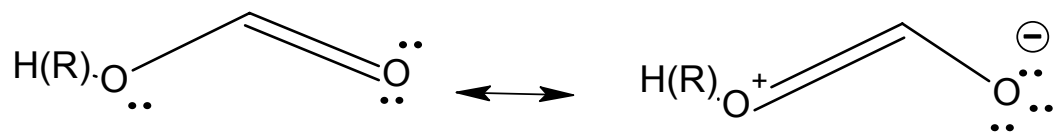
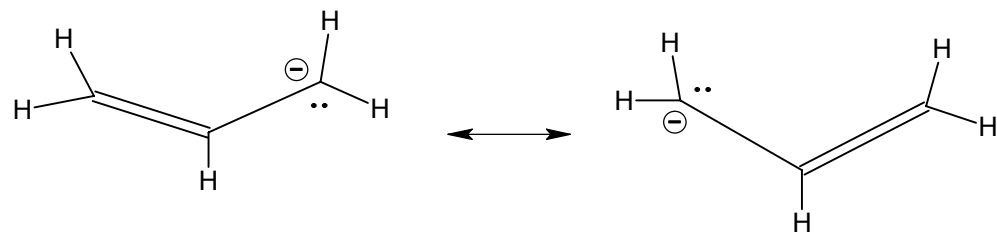
π -substituent interacts better with pure p-orbital of planar structure than with σ -out orbital of pyramidal structure

Carboanions below are planar

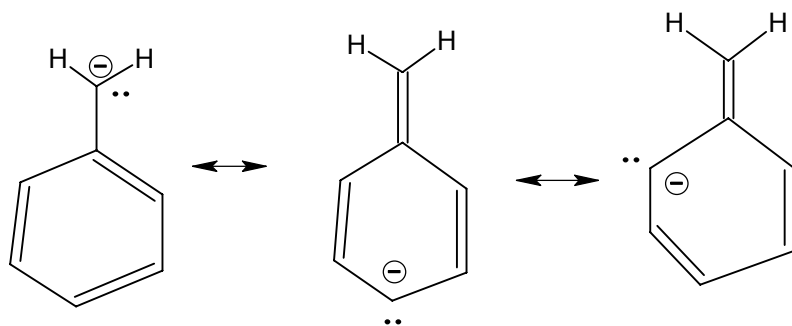


Allyl and benzyl anions are also planar- draw the resonance structures

Allyl anion and its analogs



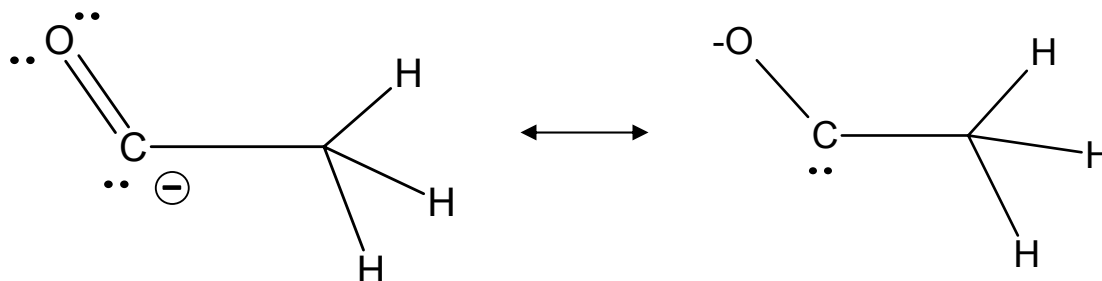
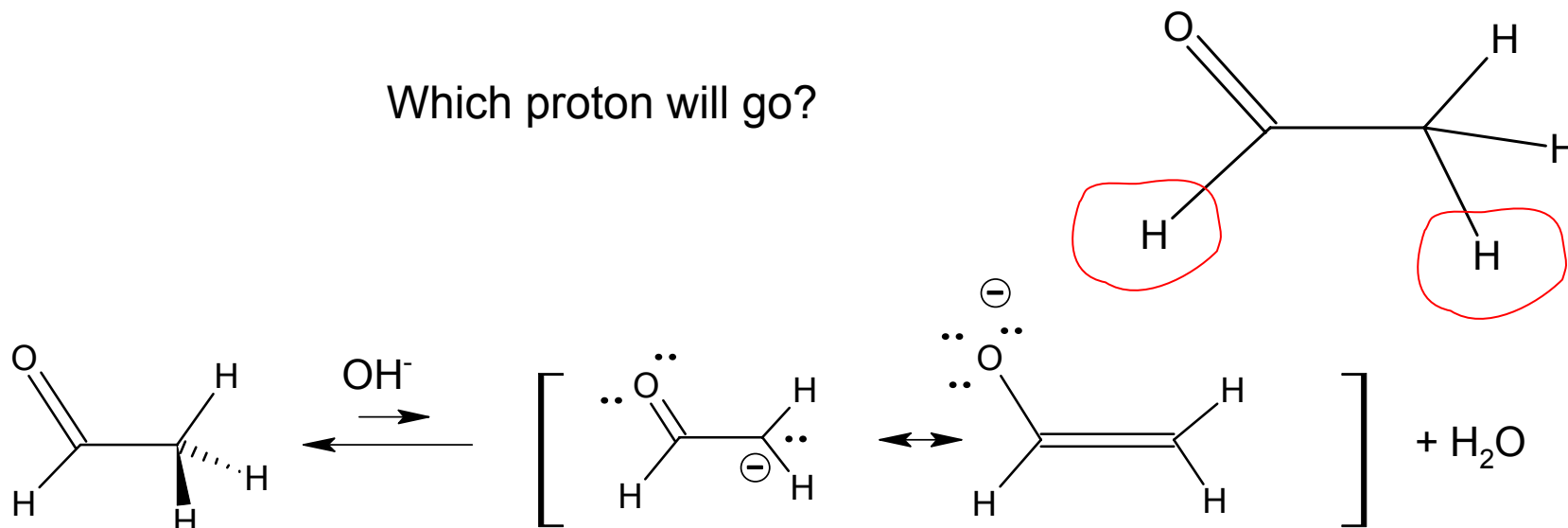
Resonance in carboxylic acids and esters



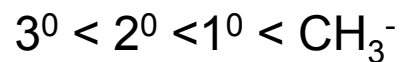
Benzyl anion

Resonance stabilization of carboanions

Which proton will go?

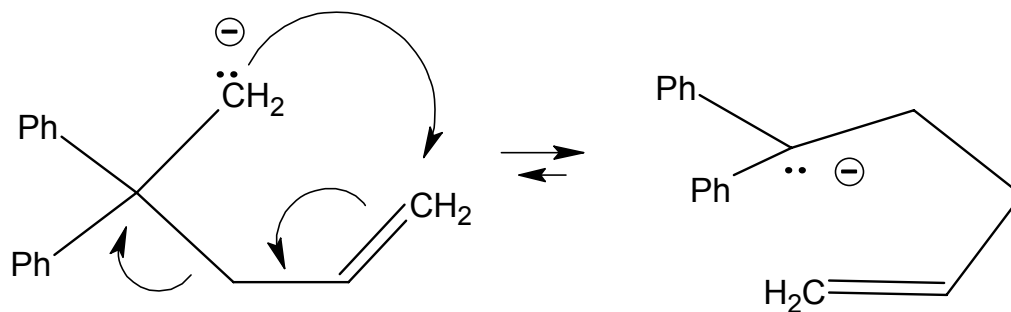


Stability of carboanions due to substituents at C

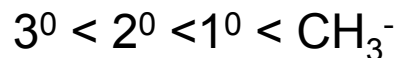


Reverse to stability of carbocations

Carboanions are less prone to rearrangements than carbocations unless the resulting structure is more stable



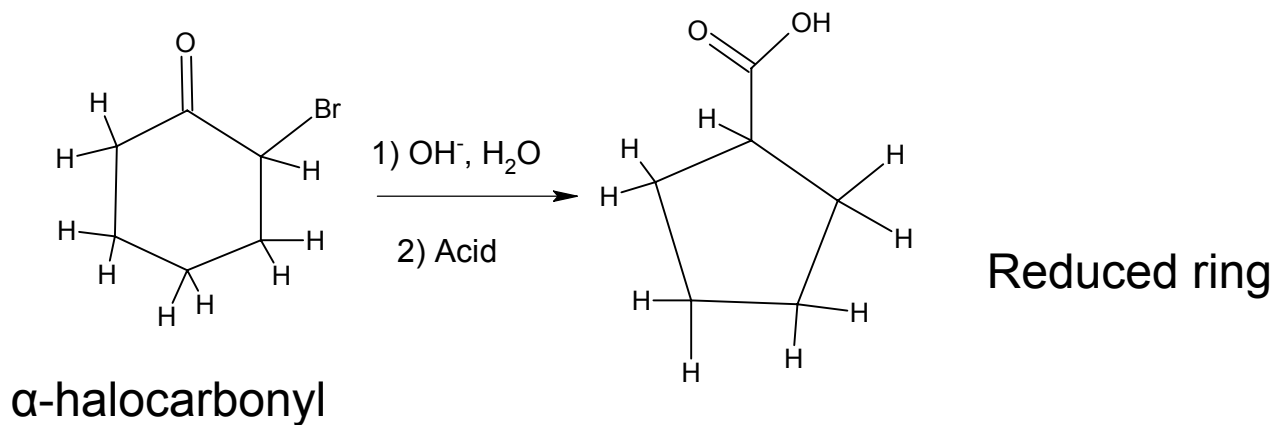
Stability of carboanions



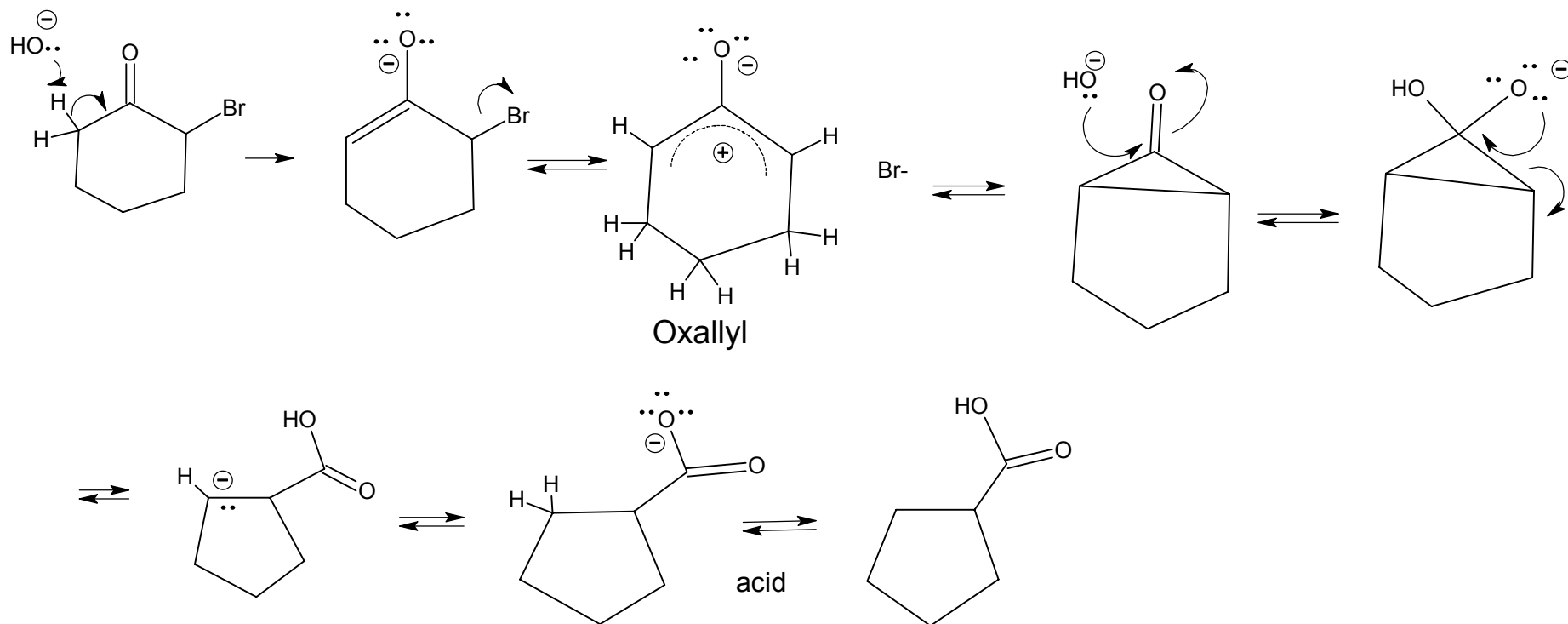
Reverse to stability of carbocations

Note that resonance stabilization may invert the trend in stabilization as shown at the above sample

Reactions involving carboanions: Favorskii rearrangement



Proposed mechanism:

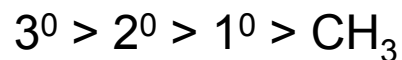


Radicals

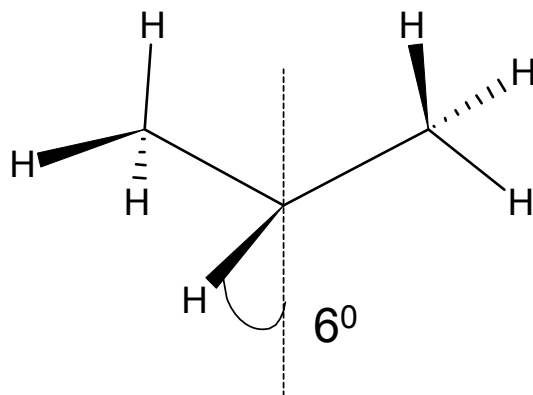
$\text{CH}_3\cdot$ D_{3h} but energetically very close to C_{3v}

CH_3 is only the planar radical- substituents shift to pyramidal form, e.g., CF_3 is strongly pyramidal

Pyramidalization and stability

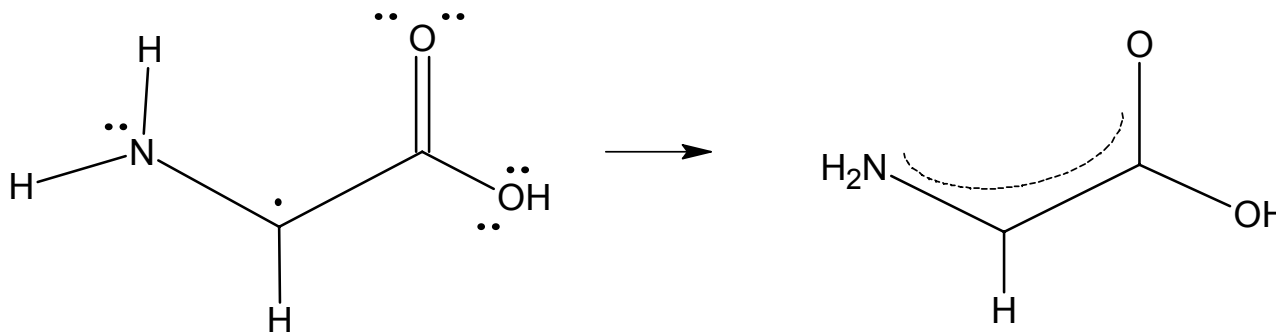


Pyramidalization decreases eclipsing interactions:



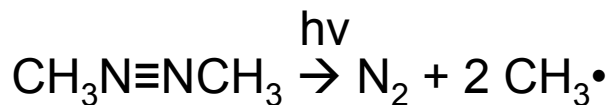
Radicals are stabilized by delocalization of unpaired electron

Capto-dative radicals: radical center resides between a donor and an acceptor- exceptional stability



The unpaired electron resides between a π -donor (the N-atom of the NH_2 group) and a π -acceptor (the carbonyl group)

Formation of radicals: homolytic cleavage (thermal or photochemical)

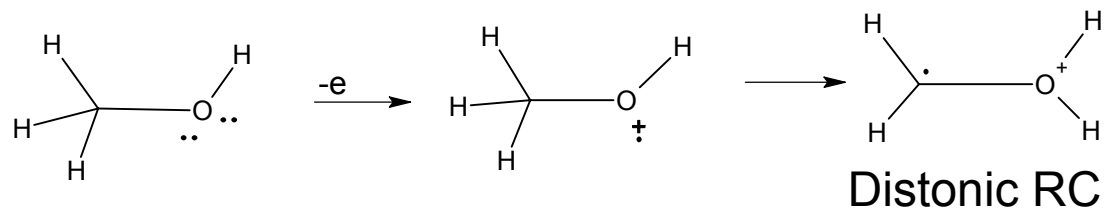


Typical chemistry- chain reactions

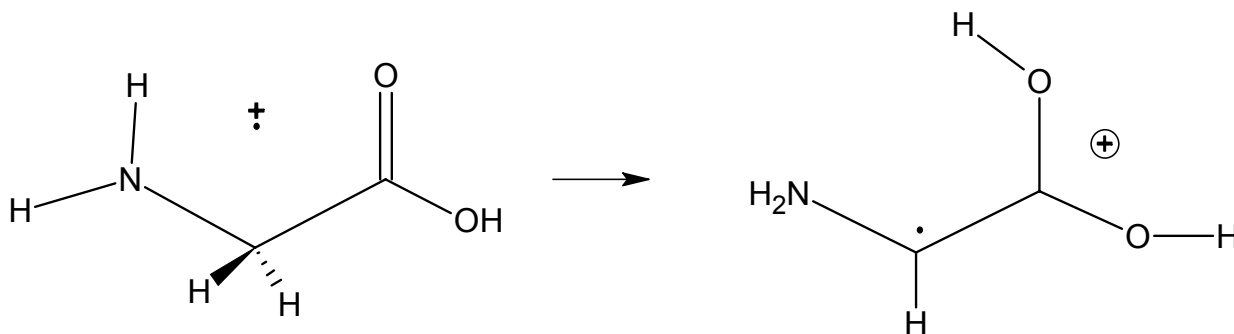
Radical cations

Remove electron from the system

Distonic radical cations (RC)- charge and spin are separated



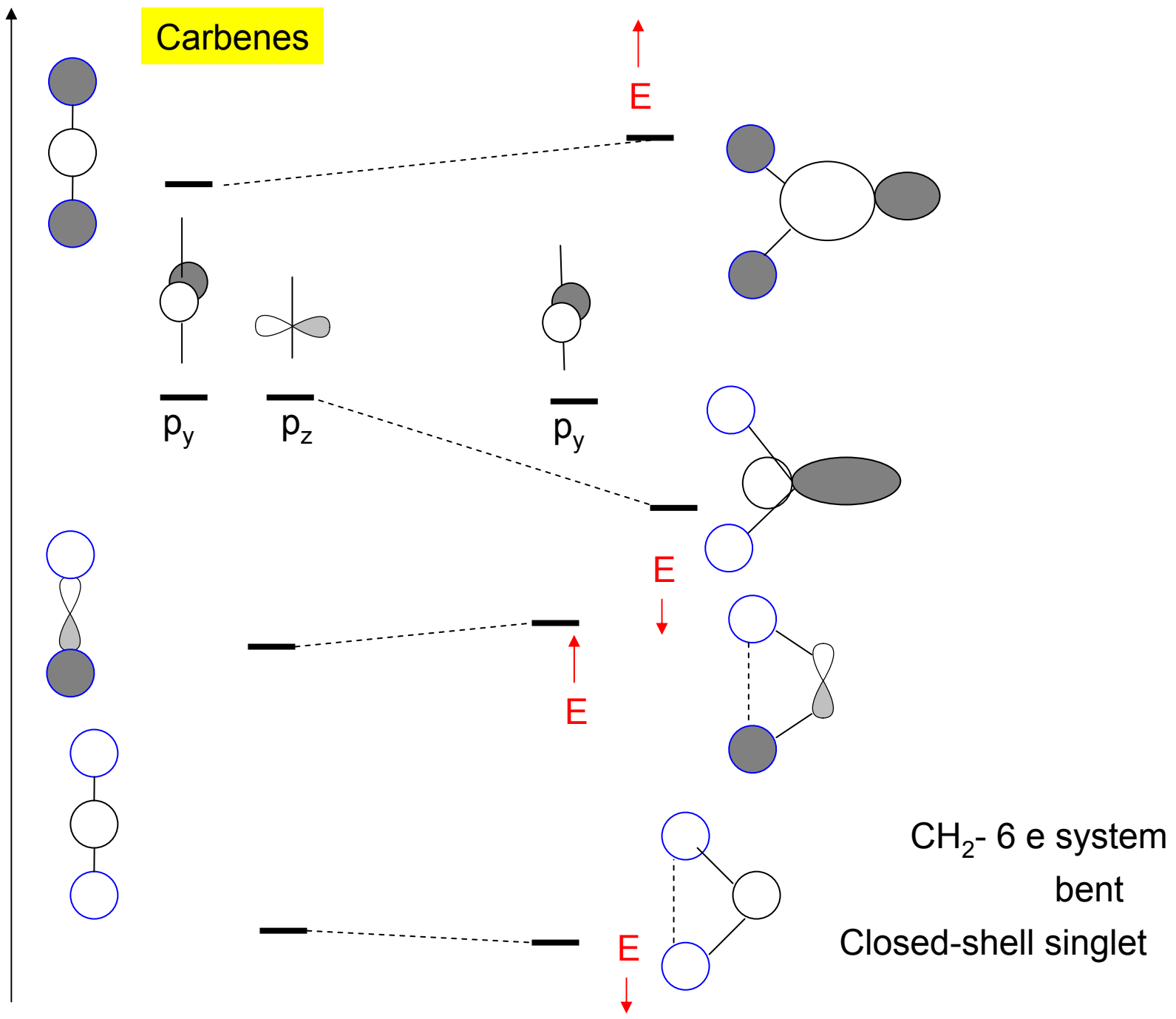
Distonic captodative RC



The unpaired electron is in fact delocalized over the main chain

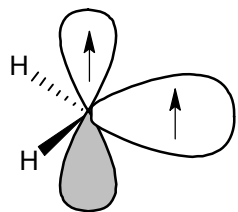
The C-H of radical cations is acidic. The carboxyl group is basic!

Carbenes

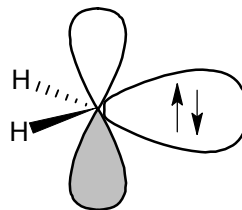


CH₂- 6 e system
bent
Closed-shell singlet

In fact, **triplet** CH₂ carbene is 9 kcal/mol lower in energy than **singlet**



Triplet
HCH=136°



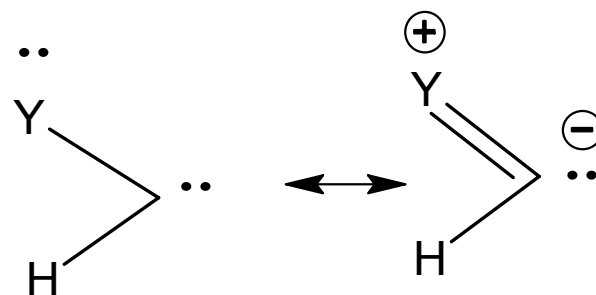
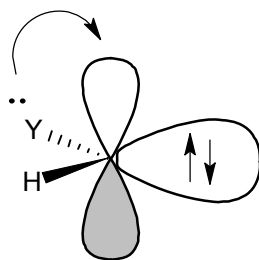
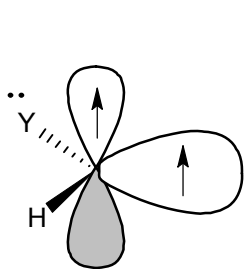
singlet
HCH=105°

How to stabilize singlet?

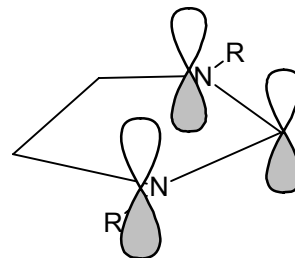
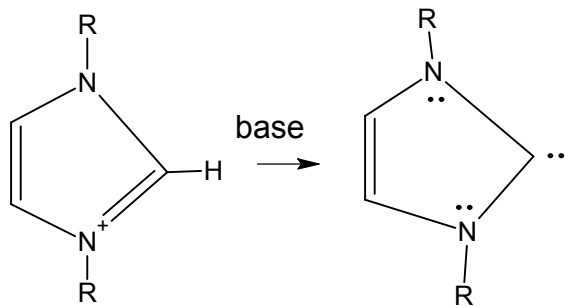
Increase bending using substituents

CF₂ – singlet is 50 kcal/mol lower than triplet

Lone-pair donation (Y=N, O..) stabilizes singlet



Stable carbenes



Orbital overlap- electronic effect

R- bulky groups- steric protection

Good ligands for Ru-based olefin metathesis catalysis

Generation of carbenes:

In singlet state

Mostly from diazoalkanes, for example



In triplet state:

Sensitization. Use a photoexcited triplet molecule $\text{S}\uparrow\uparrow$

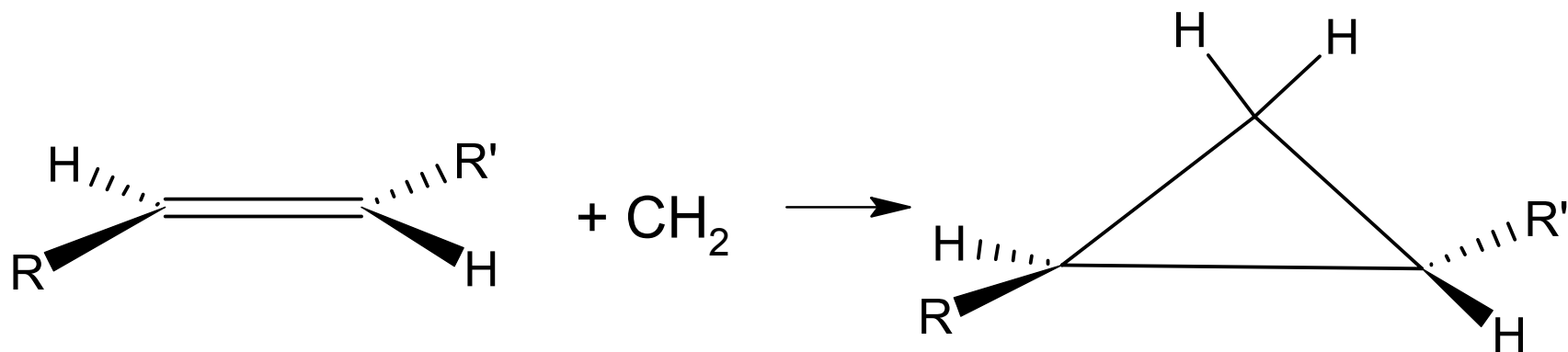


Reactions of carbenes- depend on the electronic state

Singlet carbene has empty orbital as a cation and a lone pair like an anion- combined properties

Triplet has two singly-occupied orbitals and acts more like biradical

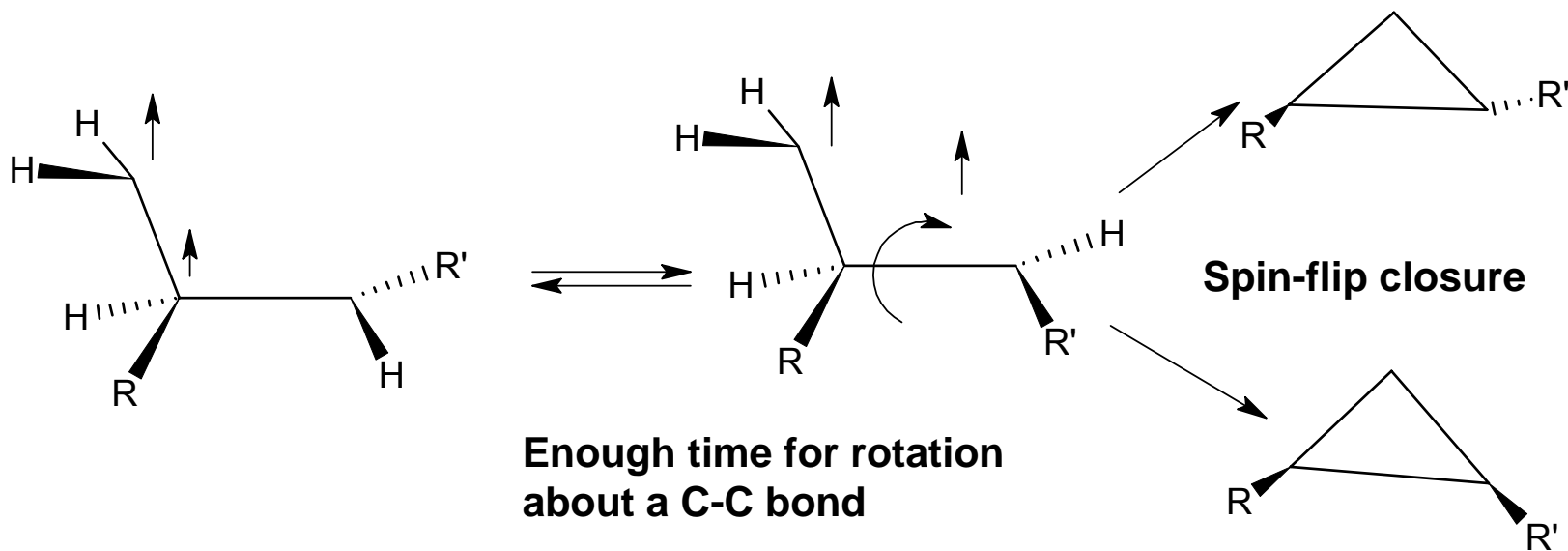
Major reaction of carbenes- cycloaddition



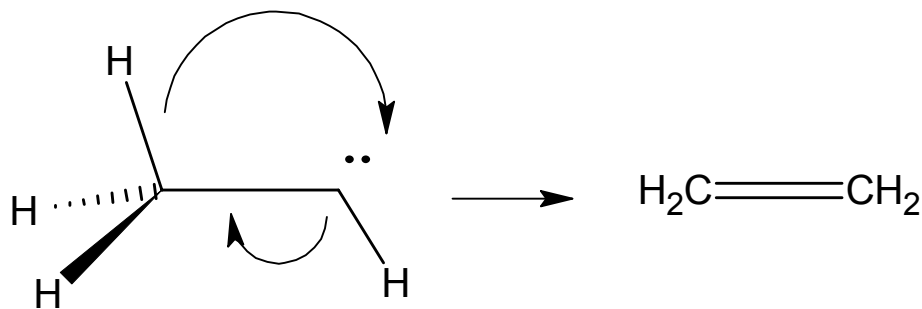
Singlet adds in one step and stereospecifically, i.e., trans- alkene gives 'trans'-cyclopropane

Triplet cannot add in one step as spin flip is needed

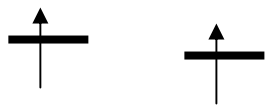
Stepwise mechanism:



1,2-hydrogen shift. The barrier is only about 0.6 kcal/mol for carbenes



Singlet Biradicals

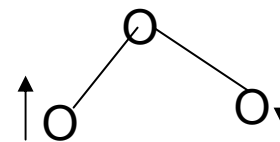


Open-shell triplet may be considered as triplet biradical



Singlet biradical has two weakly coupled electrons with opposite spin

Ozone molecule is a singlet biradical in its ground state



Many reactions go via a singlet biradical transition state

Those transition states are formed when (a) a single bond is homolitically broken, (b) a double bond is twisted; (c) a triple bond is bent

